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DIRECT DETERMINATION OF CADMIUM AND BERYLLIUM IN COAL AND FLY ASH SLURRIES USING GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY

by

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PUBLICATIONS

1. "Determination of Beryllium and Lithium in Coal Ash by Inductively Coupled Plasma Atomic Emission Spectroscopy", M.A.B. Pougnet, M.J. Orren and L. Haraldsen, Intern. J. Environ. Anal. Chem., 1985, **21**, 213-228.

2. "Direct Determination of Beryllium in Coal Slurries Using Graphite Furnace Atomic Absorption Spectrometry With Automatic Injection", Lana Haraldsen and M.A. Bruno Pougnet, Analyst, 1989, **114**, 1331-1333.

ABSTRACT

Graphite Furnace Atomic Absorption Spectrometry (GFAAS) was used for the determination of cadmium and beryllium in coal and fly ash slurries.

Sample preparation involved grinding the sample to a fine powder and slurrying it in a suitable solvent. Stable slurries were maintained by magnetic stirring during sampling. Pyrolytically coated graphite tubes were used for cadmium determinations, while beryllium was determined with platform atomisation. Ammonium dihydrogen orthophosphate and magnesium nitrate matrix modifiers were used for cadmium and beryllium determinations respectively.

Calibration graphs constructed with aqueous standards containing the appropriate matrix modifier were rectilinear to at least 100 pg cadmium and 45 pg beryllium. Results were calculated with integrated peak area measurements. The detection limits were 2.9 pg for cadmium and 0.7 pg for beryllium.

Beryllium determinations were performed with semi-automatic sample introduction. The novel semi-automatic sampling unit utilised magnetic stirring for the maintenance of stable slurries and operated with the standard Perkin-Elmer AS-40 autosampler. The principles of this unit were extended to the development of a fully automatic autosampling unit. The design and operation of both units are described.

The accuracy of the methods were evaluated by analysing standard reference materials and in some cases, comparisons with acid digestion procedures. Data ~~is~~ are presented for the analysis of South African coal and fly ash samples.

The slurry methods had acceptable accuracy and precision. In comparison with the conventional acid digestion procedures using high pressure bombs, a time-saving advantage was realised.

CONTENTS

1

INTRODUCTION

In Graphite Furnace Atomic Absorption Spectrometry (GFAAS), samples are usually analysed in liquid form and solid samples are subjected to dissolution procedures prior to analysis. Dissolution of complex samples, such as coal and fly ash, is usually accomplished by acid digestion with high pressure bombs [Dav74, Nad80, Bet86, Bet88]. Problems which have been reported with this method are:

1. Time consuming, several hours heating at elevated temperatures required, the sample preparation step thus constituting a major fraction of the total analysis time
2. Several sample manipulation steps, thus increasing the risks of contamination and analyte loss
3. Contamination of the sample solution from the metallic parts of the bomb [Bet88]
4. Incomplete dissolution [Dav74]
5. Loss of volatile elements if leakages occur
6. Number of samples which can be simultaneously processed is limited by the number of bombs available
7. Long cleaning and maintenance times
8. High cost of digestion bombs

Many of these problems can be eliminated by applying the technique of direct solid analysis. In this approach, sample preparation involves grinding the sample to a fine powder. The powder is analysed directly, with little or no further manipulation other than inserting it into the graphite tube. Direct solid analysis can also be achieved by analysing a slurry, suspension or gel prepared with the finely ground sample. Several advantages are gained by

analysing the sample directly:

1. No sample dissolution required
2. Shorter sample preparation time
3. Overall increase in sensitivity by elimination of the digestion/dilution step
4. Fewer sample manipulation steps, thus reducing risks of contamination and analyte loss
5. Fewer expensive, high purity acids required
6. Reduced analyst exposure to hazardous, corrosive materials such as hydrofluoric and perchloric acids
7. No expensive pressure vessels required for analysis of complex samples

Many researchers have recognised the advantages of direct solid analysis and applied the technique not only to GFAAS [Ebd87, Ste87, Nak88], but also to other atomic spectroscopic techniques such as Flame Atomic Absorption [Wil75, Ore77, Ful81] and Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) [Ful81, Wat86, Ebd87/2].

GFAAS is one of the most sensitive techniques for trace element analysis [Wel86]. The determination of trace levels of cadmium and beryllium in environmental samples, such as coal and fly ash, is important as both these elements are toxic.

Cadmium is readily taken up by most plants [Bau85] and may thus enter the food chain. The biological half-life is of the order of 20 years and it is becoming increasingly important to monitor cadmium levels especially as the cadmium concentration in the environment is reported to be increasing [Yin87].

Beryllium is permanently retained in mammalian tissues and the high retention can lead to pneumonites, cardiac strain

and heart disease in humans [Gel79]. This element is of no use to human metabolism and the major source of intake is by inhalation [Gel79].

The extensive use of coal in South Africa is of environmental concern as particulate matter is released into the atmosphere, especially as low grade coal with an ash content up to 25% [Ann83] is regularly used. Several studies [Dav74, Nat74, Ful83] have indicated that certain elements are more concentrated on the surfaces of the finer fly ash particles, which have a greater tendency to escape into the atmosphere, than on the coarser particles. This results in public exposure with eventual deep lung deposition [Dav74]. Contamination of surface and ground water by leachates [Ful83] is therefore also a matter for concern. Knowledge of the levels of toxic elements, such as cadmium and beryllium, in coal and fly ash is of environmental importance.

Little is known about the levels of cadmium and beryllium in South African coal and fly ashes. Watling and Watling [Wat82] determined the metal concentrations of several South African coals using Flame Atomic Absorption analysis. Values were reported for cadmium, but beryllium was not determined. Pougnet et al. [Pou85] reported on the determination of beryllium in coal ash using Inductively Coupled Atomic Emission Spectrometry.

This work investigates the application of the technique of direct solid analysis to the determination of trace cadmium and beryllium in coal and fly ash using GFAAS.

1.1 OBJECTIVES

The objectives of this study were:

1. To develop analytical procedures for the direct determination of beryllium and cadmium in coal and fly ash samples.
2. To evaluate the precision and accuracy of these methods.
3. To automate sample introduction.
4. To apply the methods to the analysis of South African coal and fly ash samples.

The following criteria were used to develop the analytical procedures:

1. The sample preparation should be kept as simple as possible with minimal manipulation.
2. Use of a single analytical procedure to determine beryllium or cadmium in both coal and fly ash samples.
3. Calibration with simple aqueous standards, thus eliminating the need for calibration with expensive solid reference standards.
4. Little or no instrumental modification should be required and standard laboratory equipment should be used. This facilitates application of the analytical procedures without the need for specialised equipment.
5. Once set up, the analyses could be routinely performed by relatively unskilled personnel.
6. The methods should have a time saving advantage over the conventional high pressure bomb acid digestion procedures.

2

DIRECT ANALYSIS OF SOLID SAMPLES IN ATOMIC ABSORPTION SPECTROMETRY

2.1 INTRODUCTION

A summary of the methods for the direct analysis of solid samples by Atomic Spectrometry is presented in table 2.1.

Table 2.1: Direct analysis of solid samples by Atomic Spectrometry [reproduced from Van80].

	Conventional	Hybrid techniques
Emission	Solid-in-flame solid-in-plasma arc spark electrothermal laser glow discharge	furnace-arc chloride generator laser-plasma furnace-plasma spark-plasma
Absorption	solid-in-flame arc spark electrothermal laser cathodic sputtering	capsule-in-flame hollow graphite "T" tube furnace-flame arc/spark-flame chloride generator
Fluorescence	laser laser-spark electrothermal	furnace-flame

A comprehensive discussion on all the atomic spectrometric techniques is beyond the scope of this work and this chapter will focus on Atomic Absorption Spectrometry with particular reference to electrothermal atomisation (GFAAS) and, to a lesser extent, flame atomisation.

For further information, comprehensive reviews can be consulted. Van Loon [Van80] reviewed the applications of direct solids analysis in Atomic Absorption, Fluorescence and Emission Spectrometry. Headridge [Hea80] reviewed the direct analysis of metal samples using GFAAS. Various aspects of the application of the technique in Atomic Absorption Spectrophotometry were reviewed by Langmyhr and

Wibetoe [Lan85]. Extensive lists of materials analysed and elements determined are included.

2.2 SAMPLES ANALYSED IN ATOMIC ABSORPTION SPECTROMETRY

The types of solids which have been analysed in Atomic Absorption Spectroscopy include [Lan85/2]:

Powders
Powders suspended in solid, liquid or gaseous dispersing agents
Drillings or turnings
Fibers
Sheets or foils
Cells of biological origin
Tissues of human, animal or plant origin
Insects and insect egg

Materials in liquid form e.g. biological fluids, can also be analysed by transforming them into solids by drying, dry ashing, plasma ashing or lyophilisation [Lan85/2].

A large number of elements in various matrices have been determined by AAS. In their review, Langmyhr and Wibetoe [Lan85] cited 458 references and concluded that "47 elements have been determined, and that all types of materials can be analysed".

2.3 FLAME ATOMIC ABSORPTION ANALYSIS OF SOLID SAMPLES

In 1962, Gilbert [Gil62] reported the first experiment on the direct atomisation of solids in the flame where he measured the emission spectra of a soil suspension slurried in 1:1 glycerol-isopropanol.

Nebulisation of suspended solids has subsequently been applied to atomic absorption analysis. Harrison and Juliano [Har71] reported on the determination of tin in different tin compounds. Large bore Beckman total consumption burners

were used for the aspiration of suspensions in the hydrogen and acetylene flames. Willis [Wil75] investigated factors affecting atomisation efficiency when suspensions of geological materials were aspirated into the flame. He found that only particles below 12 μm contributed significantly to the observed signal. O'Reilly and Hale [Ore77] aspirated coal slurries into an air/acetylene flame.

The conventional capillary pneumatic nebuliser requires the sample to pass through a small (about 0.36mm) capillary orifice [Fry77]. With slurries and high salt samples, blockage can be a serious problem. Fry and Denton [Fry77] introduced the first nebuliser based on the Babington principle. The design of this nebuliser is such that only gases pass through an orifice, the sample having a relatively unrestricted flow. The Babington principle has also been applied to the design of the "V" groove nebuliser. Figure 2.1 illustrates the design of these nebulisers. These nebulisers have been used for the nebulisation of suspensions and slurries by flame AAS as well as ICP-AES [Orr85, Ebd87/2].

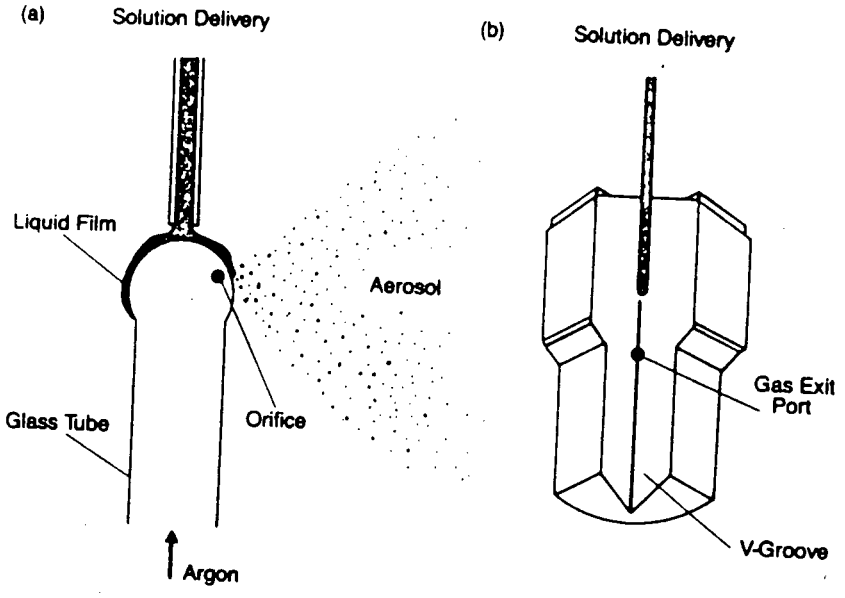


Figure 2.1: (a) Babington nebuliser
(b) V-groove nebuliser

(reproduced from Bro84)

The number of devices reported in the literature for the introduction of powdered samples into the flame is limited. The use of a miniature graphite or metal cup containing the sample to be analysed has been reported [Ves77]. The crucible was held in a mechanism for moving the cup in or out of the flame. Introducing the sample between the threads of a steel screw has also been reported [Gov71].

Standardisation is difficult as atomisation efficiency is dependent on particle size [Wil75]. As pointed out by Langmyhr and Wibetoe [Lan85], the direct analysis of solids using the flame is not to be recommended when a high degree of accuracy is required, but that the technique is useful for geochemical prospecting and for determining wear metals in oils.

2.4 FURNACE ATOMIC ABSORPTION ANALYSIS OF SOLID SAMPLES

Metal atomisation cells, usually tantalum or tungsten, have been used for electrothermal atomisation, but now most atomisers are made of graphite [Lan85]. The preferred commercial cell shape is a tube, but cells in the form of "T" [Nic78], "+" [Tal72] and cup cells [Lun79] have been reported.

Introduction of powdered samples into the furnace has been achieved by inserting small boats of metal or graphite into the tube. The contents of the boat are deposited in the tube, the boat removed and reweighed. Alternatively the graphite boats may be left in the furnace. The construction of some instruments make the insertion of samples through the end of the tube inconvenient. In these cases, the samples have to be introduced through the sample introduction port. This can be achieved by utilising

commercially available solid sample injectors such as the one manufactured by Perkin-Elmer (see Chapter 3).

Slurries, suspensions and gels have been introduced using conventional pipettes used for liquid samples.

2.4.1 Samples analysed

The technique has been applied to a wide range of samples including geological [Nak88, Dek87], biological [Gro81, Her85, Wel86, Ats87, Ebd87], metallurgical [Lun79], foodstuffs [Ste87] and soil [Jac83, Hin85, Hin88].

Table 2.2 summarises the recent work on the direct determination of elements in coal and fly ash. A few examples of the direct determination of cadmium and beryllium in various matrices appear in table 2.3.

2.4.2 Problems of direct solid analysis

In the direct analysis of solid samples, the intact matrix is deposited in the tube. Sample drying, destruction of the matrix (ashing) and atomisation all occur in situ, ie. the entire analytical work is done on the instrument. The problems which occur with this technique may differ considerably from those experienced with the analysis of liquid samples. Some of the problems which have been associated with the method are [Ret86, Ste85]:

- -sampling errors
- -background absorption interferences
- -sample dependent peak shapes
- -buildup of residual material in the tube
- -standardisation

Table 2.2: Direct analysis of coal and fly ash

Elements determined	Matrix	Slurry/ solid	Tube	Calibration	Comments	Reference
Be	Coal	Slurry	Platform	Aqueous standards	Automated sample introduction Magnesium nitrate matrix modifier	Har89
Cu, Cr, Ca, Fe, Mn, Pb V	Coal	Slurry	Platform	Peak area Aqueous standards	Automated sample introduction	Mil88
Se	Coal	Slurry	Pyrolytically coated	Aqueous standards	Slurry medium: nickel nitrate/nitric acid/ ethanol Air ashing	Ebd88
Cd, Ni	Coal, fly ash	Solid	Cup in tube	Peak area Cd: aqueous standards Ni: solid reference	Oxygen ashing for coal Cd:phosphate modifier Ni:magnesium nitrate modifier	Sch87
Se	Fly ash	Solid	Graphite boat	Peak area Aqueous standards		Due87
As	Coal	Slurry Thixotropic slurry	Pyrolytically coated cuvettes	Aqueous standards	Slurry medium: nickel nitrate/magnesium nitrate/ nitric acid/ethanol	Ebd87/3
Cu, Pb	Fly ash	Solid	Graphite cup	Peak height Aqueous standards	Atomisation from Ta insert containing condensed analyte	Ret86
As	Coal	Solid Slurry	Uncoated tubes	Aqueous standards Solid standards	Slurry medium: nickel nitrate/magnesium nitrate/ nitric acid/ethanol	Ebd82/2
Cu, Ni, V	Coal Petroleum coke	Solid	Graphite tubes Pyrolytically coated and uncoated	Aqueous standards Solid reference standards		Lan80
Be	Coal	Solid	Graphite tube	Aqueous standards: calibration graph and standard addition		Gla77

Table 2.3: Determination of cadmium and beryllium in solid samples

Elements determined	Matrix	Slurry/ solid	Tube	Calibration	Comments	Reference
Cd, Pb	Biological	Solid	Platform	Aqueous standards Solid reference standard	Design of new solid sampling tube and platform	Bro87
Cd	Biological	Slurry	Platform	Aqueous standards	Ammonium dihydrogen orthophosphate matrix modifier	Ebd87
Cd	Vegetable Protein foodstuffs Single cell protein	Suspension	Pyrolytically coated	Aqueous standards	Oxygen ashing Ammonium dihydrogen orthophosphate matrix modifier Automatic sample introduction	Ste87
Cd, Pb, Zn	Biological	Solid	Graphite boat	Aqueous standards		Str87
Cd, Cr, Cu, Pb, Mn	Hay	Solid	Cup-in-tube	Aqueous standards		Völ85
Cd	Biological	Solid	Platform	Aqueous standards		Her85
Cd, Pb	Soil	Slurry	Platform	Aqueous standards	Samples slurried in water	Hin85
Cd	Wheat flour	Solid	Graphite tube	Aqueous standards	Mechanised sample introduction	Gro82
Cd, Ag, Bi, Zn	Steel	Solid	Graphite cup	Solid standards	Automatic sample introduction	Lun79/2
Be, Cd, Se, Ag, Hg, Pb	Simulated airborne particulates		Atomisation from graphite tube used for sample collection	Aqueous standards		Sie74
Be	Simulated airborne particulates		Atomisation from graphite tube used for sample collection	Aqueous standards collected on sample tubes		Sie73

Sampling error can be reduced to an acceptable level by adequate sample grinding [Lan85/2]. Other problems have been overcome by ashing in an oxygen or air atmosphere [Ste87, Ebd88], use of background correction systems such as the Zeeman [Her85, Völ85] or Smith-Hieftje [Ebd88] systems and use of the stabilised temperature platform furnace (STPF) technology [Ebd87]. Often a combination of these is used.

The deuterium and tungsten lamps introduce errors when the broad band systems contain fine-structure or when foreign absorption lines are contained in the bandpass [Lan85]. These background correctors are only capable of compensating for a certain amount of non-specific absorption and analysis of certain solid samples (eg. biological) often overtax the system [Kur85]. In recent years, the Zeeman and the Smith-Hieftje systems have been introduced. The Zeeman system is based on the splitting of atomic lines in a strong magnetic field. The Smith-Hieftje system is based on the broadening and self-reversal of the emission line when the power of the hollow cathode lamp is increased to high levels for a short while. These systems have been used to overcome many of the problems experienced with deuterium arc background correction [Wel86, Let87].

Development of the Stabilised Temperature Platform Furnace technique has had important implications for direct solid analysis as well as for GFAAS in general. A brief overview of the principles will be given.

2.4.2.1 Stabilised temperature platform furnace technique (STPF)

Pulse operated furnaces based on the Massmann design, such as the Perkin-Elmer HGA system, inherently suffer from temporal non-isothermality as well as spatial non-

isothermality along the length of the tube [Mat81]. L'vov [Lvo78] demonstrated that many interferences reported in GFAAS arise from non-uniform temperature in the furnace. To overcome these problems, he proposed the insertion of a graphite platform inside a pulse operated furnace.

The platform is heated primarily by radiation from the tube walls, therefor its temperature is delayed relative to the graphite tube. Sample vaporisation and atomisation will be delayed until the tube has more nearly reached constant temperature conditions. These effects are illustrated in figure 2.2. Many vapour phase interferences occur when samples are vaporised from the hot tube wall into a cooler gas atmosphere. With platform atomisation, the time delay realised permits atomisation into a gas at a higher temperature. At the higher temperature the equilibrium is shifted towards the formation of free atoms, thus reducing interference effects [Fer81].

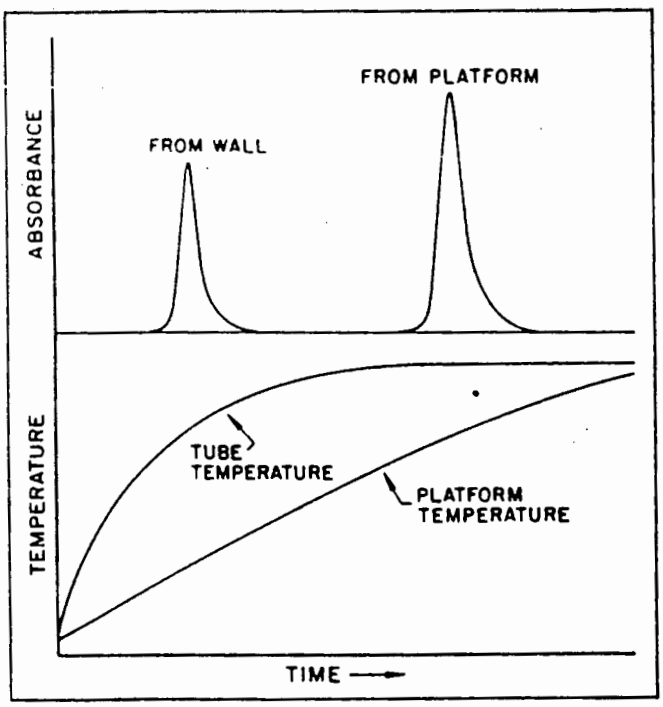


Figure 2.2: Effect of tube temperature on analytical signal. Sampling off tube wall and platform.

(reproduced from Fer81)

Kurfürst [Kur85] reviewed solid sample tube insertion systems in terms of the practical aspects of sample introduction as well as the ability to function as a L'vov platform. Systems such as the microboat, platform boat, miniature cup and central probe were evaluated. He concluded that only the platform boat met the requirements for solid sample handling and functions as a L'vov platform.

"Matrix modification" [Edi75] is a term used to describe chemical treatment of samples which results in the formation of a more stable analyte compound, thus raising the appearance temperature. It was pointed out by Chakrabarti et al. [Cha80], that the technique should be called "analyte modification" since it is the analyte which is converted to a less volatile compound.

The STPF used in conjunction with matrix modification has been reported to reduce interferences [Kai81, Fer81, Man83, Ebd87] and allows integrated peak area determination thus yielding more accurate results.

2.4.3 **Automation of sample introduction**

The analysis of slurries or suspensions in GFAAS has a number of advantages over the direct powder method of analysis. Conventional pipettes are used for sample introduction. Powder analyses generally require weighing before and after sample deposition, the mass delivered being determined by difference. Automation of slurry introduction is possible as the principles of sampling ~~is~~ are the same as for liquids. Powder sampling is more difficult to automate due to the vast number of different types of powder that have to be analysed.

Lundberg and Frech [Lun79/2] reported on the application of an autosampler for the determination of cadmium, bismuth and

zinc in solid steel samples. The Varian Techtron ASD-53 autosampler was modified to dispense the samples. The capillary tubing used to dispense liquid solutions was replaced by a stainless steel tube. Platinum gauze was attached to the sampling end of the tube to retain the samples. A vacuum pump was connected to the other end of the tube. The samples were contained in polyethylene sample vials loaded into the sample carousel of the autosampler. The sampling program proceeded automatically until all the samples were analysed. Switch over between solid and liquid sample introduction could be achieved in less than one minute with this modification.

Few reports on the automatic introduction of slurries and gels are found in the literature. Stephen et al. [Ste85] injected spinach suspensions with an AS-40 autosampler. The authors found that solution droplets frequently remained attached to the capillary tube and dropped onto the inside tube wall thus impairing analytical precision. The problem was solved by careful adjustment of the capillary position and frequently cleaning the tube with acetone. Ebdon and Parry [Ebd87/3] reported on the injection of thixotropic coal slurries by an autosampler. Slurries were found to be stable for up to 24 hours but poor reproducibility due to ineffective expulsion of the slurry from the pipette tip was obtained. The authors suggest that a pneumatically operated auto-sampler would be more suitable.

Miller-Ihli [Mil88] reported on the simultaneous multi-element GFAAS analysis of NBS SRM slurries using an AS-40 autosampler. Two approaches to the use of this autosampler were undertaken. In the first, the slurry preparation was vortexed and an aliquot of the sample withdrawn and placed into the autosampler cup, the cup being placed on the autosampler tray just in time for the sample to be withdrawn. The second approach was to mix an aliquot of the

sample in the autosampler cup by insertion of an ultrasonic probe. As pointed out by the author, operator attendance is necessary and the method does not permit automated mixing which would be required for routine analysis. The author also reported on the use of ~~an~~ a prototype mixing tray accessory for the AS-40 autosampler which utilises ultrasonic agitation. Decreasing absorbance values were observed for Fe, Cr and Al in NBS spinach leaves (SRM 1570), which was attributed to inefficient agitation.

Epstein et al. [Eps89] reported on the use of a prototype ultrasonic probe mixer after the design of Miller-Ihli [Mil88]. This was synchronised to the operation of the Perkin-Elmer AS-60 autosampler. This system was used for the analysis of a river sediment standard reference material (SRM 2704). The sample could be weighed directly into the autosampler cup to which the slurrying solution was added. All sources of experimental variability were examined. It was concluded that the accuracy and precision of the results were highly dependent on analyte homogeneity and that the slurry sample introduction system adequately suspends the solids for sampling.

2.5 THE FUTURE OF THE DIRECT ANALYSIS OF SOLID SAMPLES IN GFAAS

Several problems associated with direct analysis of solids have been reported but these must be viewed against the demands placed on the analytical technique. The intact sample, with little or no modification other than grinding, is presented for analysis.

The large number of research papers on the application of the technique of direct solid analysis indicate that it is progressing past the stage of being a novel technique used only in research institutions. Further indication is given

by the publication of papers dealing with the more practical aspects of the technique [Kur85, Kur87] as well as reports on industrial applications [Ess87].

Esser [Ess87] discussed the applications of solid sampling in German industries up to 1986. The matrices included food products, plastics, and various organic and inorganic matrices. Cadmium was the most-determined element, followed by lead, due to the toxicity of these elements. The concentrations of the elements determined ranged from the % level to near detection limits. The accuracy requirements were very different. Very accurate results were required for cadmium and lead determinations in baby food, whereas one-shot-monitoring of cadmium was sufficient for plastics analysis.

A survey of the literature reveals that the advantages of the direct analysis of solid samples had led to the application of the technique to the determination of a wide range of elements in a variety of matrices. GFAAS has proved useful for trace element analysis especially when fast sample output is required, or limited sample masses are available. Commercial availability of automated systems for sample introduction may lead to an even wider acceptance of the technique.

3

EXPERIMENTAL

3.1 EQUIPMENT

Atomic absorption determinations were made on a Perkin-Elmer model 5000 Atomic Absorption Spectrophotometer equipped with a HGA 500 Graphite Furnace/Programmer and connected to a Facit printer. Absorbance peaks were recorded with a PE model 56 strip chart recorder.

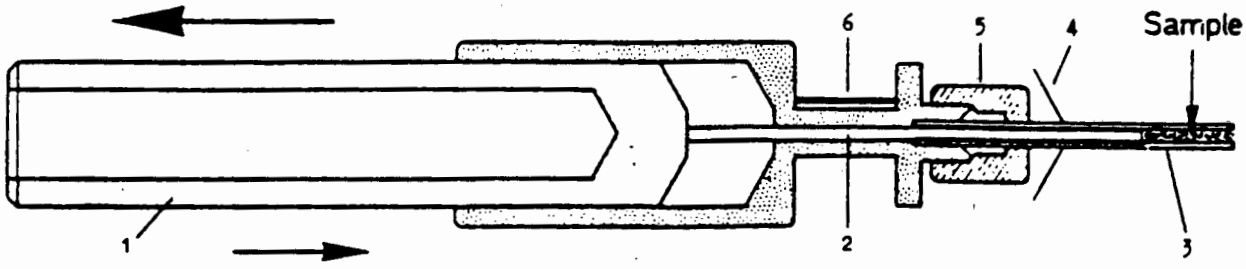
The spectrophotometer background correction system employs a deuterium arc lamp for the 190 to 350nm region and a tungsten halide lamp between 350 and 900nm. Further details on the operation of the spectrophotometer and furnace programmer appear in Appendix I.

An AS-40 Autosampler/Sequencer was modified to automatically dispense slurry samples (see section 3.7.1). Manual injection of liquids and slurries were performed with Gilson pipetman^{R} automatic pipettes.

Solid samples were introduced directly into the furnace with a Perkin-Elmer powder sampler (part number 112 132) illustrated in figure 3.1. It operates in a similar manner to an automatic pipette. A PTFE plunger rod (2) is moved forward or backward in a glass capillary (3) by the plunger (1). The plunger has a number of detent positions ("click stops") to allow for the sampling of differing masses. The sampler is charged by withdrawing the plunger to one of its click stops and repeatedly pushing the glass capillary into the sample until the capillary is full. The cleaning cuff (4) is drawn over the capillary to remove sample residues from the outside of the capillary. The sampler is weighed before and after sample introduction to obtain the mass dispensed.

The internal and external purge gas was high purity argon ("Spec Arg", Air Products, South Africa (Pty) Ltd.). The

alternate gases for certain applications were medical air (purified air, containing 20.5 to 21.5% oxygen) and oxygen (both from Afrox Ltd.).



1. Plunger
2. Plunger rod
3. Glass capillary
4. Cleaning cuff
5. Nut
6. Pin (clips onto AS-40 sampling arm)

Figure 3.1: Powder sampler (reproduced from Perkin-Elmer).

A Perkin-Elmer Intensitron^{R} hollow cathode lamp was employed for cadmium determinations. The beryllium hollow cathode lamp was obtained from S&J Juniper & Co. Pyrolytically coated tubes, uncoated tubes and L'vov platforms were obtained from Perkin-Elmer.

Samples were ground with a Fritsch^{R} Pulverisette micro mill (an agate ball mill). Particle size analyses were performed with a Malvern Model 2600 HSD Particle Sizer (Malvern Instruments, Malvern, England). Samples were weighed with a Mettler (electronic) or Sartorius (manual) balance and a Bransonic 521 ultrasonic bath was used for sample sonication.

Parr^R (model 4745) teflon-lined acid digestion bombs were used for sample digestion.

3.2 REAGENTS

Milli-Q (Millipore^R) water was used throughout.

Hydrofluoric acid (48%) and nitric acid were Aristar^R grade (BDH). Triton X-100 (iso-octylphenoxypolyethoxyethanol polyethoxy chain) and magnesium nitrate ($Mg(NO_3)_2.6H_2O$) were obtained from BDH. Ammonium dihydrogen orthophosphate ($NH_4H_2PO_4$) pro analysi grade was obtained from Merck.

3.3 SAMPLES AND STANDARDS

3.3.1 Samples and standard reference materials

Powdered coal and fly ash samples were obtained from various power stations throughout South Africa. Abbreviations used are as follows:

Power stations:

AR	Arnot
CA	Camden
DU	Duvha
HE	Hendrina
KO	Komati
KR	Kriel
MA	Matla
WI	Wilge

Other:

LH/RH	Left/Right hand precipitator
LHE/LHE	Left/Right hand economiser
F	Field
PR	Precipitator
T	Test
BLR	Boiler
PFA	Pulverised fuel ash (fly ash)
PF	Pulverised fuel (coal)

The following samples were analysed:

Sample number	Description	Sample number	Description
1	AR BLR4 PFA RH1 PR	57	MA BLR1 PFA RH5 PR
2	AR BLR4 PFA RH2 PR	58	MA BLR1 PFA RH6 PR
4	AR BLR4 PFA LH2 PR	59	MA BLR1 PFA RH7 PR
6	CA BLR4 PFA LH1 PR	60	MA BLR1 PFA RH8 PR
9	CA BLR4 PFA RH ECON	66	MA2T PFA RH1 PR
13	CA BLR6 PFA LH2 PR	67	MA2T PFA RH2 PR
15	CA BLR6 PFA RHE PR	68	MA2T PFA RH3 PR
18	DU BLR1 PFA LH ROW2 PR	69	MA2T PFA RH4 PR
19	DU BLR1 PFA LH ROW3 PR	87	AR BLR4 PF
20	DU BLR1 PFA LH ROW4 PR	88	CA BLR4 PF
21	DU BLR1 PFA RH ROW1 PR	89	CA BLR6 PF
23	DU BLR1 PFA RH ROW3 PR	90	DU BLR1 PF
34	KO BLR7 PFA PR	91	HE BLR5 PF
42	KR BLR6 PFA 2 PR	92	HE BLR6 PF
45	MA BLR1 PFA LH1 PR	93	KO BLR1 PF
46	MA BLR2 PFA LH2 PR	94	KO BLR2 PF
47	MA BLR1 PFA LH3 PR	95	KO BLR6 PF
48	MA BLR1 PFA LH4 PR	96	KO BLR7 PF
49	MA BLR1 PFA LH5 PR	97	KO BLR8 PF
50	MA BLR1 PFA LH6 PR	98	KO BLR9 PF
51	MA BLR1 PFA LH7 PR	99	KR BLR1 PF
53	MA BLR1 PFA RH1 PR	100	KR BLR6 PF
54	MA BLR1 PFA RH2 PR	101	MA BLR1 PF
55	MA BLR1 PFA RH3 PR	102	WI BLR6 PF
56	MA BLR1 PFA RH4 PR	103	WI BLR9 PF

NBS Standard Reference Materials were obtained from the U.S. Department of Commerce, National Bureau of Standards (now known as National Institute of Standards and Technology), Washington D.C., 20234:

NBS SRM 1635: Trace elements in coal (subbituminous)
NBS SRM 1632a: Trace elements in coal (bituminous)
NBS SRM 1633a: Trace elements in coal fly ash

South African Reference Materials (SARM) were obtained from the Council for Mineral Technology (MINTEK), Private Bag X3015, Randburg, 2125, South Africa:

SARM 18: Bituminous (from Witbank)
SARM 19: Subbituminous to bituminous (from the Orange Free State)
SARM 20: Subbituminous to bituminous (from Sasolburg)

Prior to grinding, fly ash samples were dried at 105°C for at least one hour and coal samples for a minimum of two hours. The reference standards were dried according to the procedures specified on the certificate of analysis.

3.3.2 Standard solutions and blanks

Working standards were prepared daily by serial dilution of stock standard solutions (beryllium sulphate Spectrosol^R and cadmium nitrate Spectrosol^R, BDH). Reagent blanks were prepared for all analyses.

3.4 GRINDING PROCEDURES

The dried samples (4 to 5g) were ground for 2 hours in the Fritsch^R micro mill using the interrupt facility. Samples were stored over silica gel in a desiccator.

3.5 CLEANING PROCEDURES

All glassware and sample containers were soaked for at least 24 hours in a 10% solution of Contrad (a detergent obtained from BDH) followed by rinsing with Milli-Q water and overnight soaking in 10% nitric acid. After final rinses with Milli-Q water, the glassware and containers were allowed to air-dry.

Plastic pipette tips used for cadmium determinations were soaked in 10% nitric acid prior to their use.

The agate ball mill was rinsed with Milli-Q water, then acetone, followed by a final rinsing with Milli-Q water. The mill was then "dry-cleaned" with a small amount of the sample to be ground.

3.6 ANALYTICAL PROCEDURES

3.6.1 Parr bomb digestion of fly ash for beryllium determinations

Approximately 0.02g sample was weighed into a teflon cup. 1ml of nitric acid and 3ml of hydrofluoric acid were added. The cup was capped and placed into the stainless steel digestion bomb which was sealed and heated at 115 °C for 4 hours. After cooling, the digested solution was quantitatively transfered to a 50ml polypropylene flask and diluted to volume with Milli-Q water.

The spectrophotometer and furnace conditions are outlined in Table 3.1.

The samples were analysed by the standard addition method. Pyrolytically coated graphite tubes with "home-made" platforms (see chapter 5) were used. 20μl sample volumes were manually injected.

Table 3.1: Operating conditions for the determination of beryllium in digested samples using GFAAS.

(a) Spectrophotometer

Wavelength (nm):	234.9
Slit width (nm):	0.7
Lamp current (mA):	8
Background corrector:	On
Integration time (seconds):	6

(b) Furnace

Step	Temperature °C	Ramp (seconds)	Hold (seconds)	Internal argon flow (ml/min)
Dry	180	10	40	300
Ash	1000	10	20	300
Atomise	2700	0	5	100
~~Cleam~~ clean	2700	1	3	300
Cool	20	2	10	50

3.6.2 **Slurry analysis**

The spectrophotometer and furnace operating conditions appear in table 3.2.

3.6.2.1 Sample preparation for cadmium determinations

An appropriate mass of the sample (approximately 0.4 to 1.0g of coal and 0.02 to 0.20g of fly ash) was transferred to a 10ml volumetric flask. 0.5ml of ethanol and 8ml of matrix modifier solution were added. The flask was placed in the ultrasonic bath for 5 minutes and diluted to volume with matrix modifier solution. The slurry was shaken well and transferred to a 15ml glass vial containing a PTFE coated magnetic stirrer bar. The slurry was stirred during sampling. 25μl aliquots were manually injected into the furnace.

Table 3.2: Operating conditions for analysis of coal and fly ash slurries

(a) Spectrophotometer

Element	Cadmium	Beryllium
Wavelength (nm):	228.8	234.9
Slit width (nm):	0.7	0.7
Lamp current (mA):	6	8
Background corrector:	On	On
Integration time:	6	8
Tube:	Pyrolytically coated	Pyrolytically coated with pyrolytic platforms

(b) Furnace

Element	Step	Temperature °C	Ramp (seconds)	Hold (seconds)	Internal argon flow (ml/min)
Cd[a]	Dry 1	60	10	10	300
	Dry 2	120	20	20	300
	Ash	700	40	30	300
	Atomise	1300	0	4	50
	Clean	2700	2	5	300
Be[b]	Dry 1	60	10	10	300
	Dry 2	120	5	20	300
	Ash	1600	20	20	300
	Atomise	2700	0	6	50
	Clean	2700	1	5	300
	Cool	20	2	10	50

a Samples slurried in a solution containing 20g $NH_4H_2PO_4$ per litre of 0.005% Triton X-100 containing 0.2% (v/v) of ca. 65% HHO_3. 0.5ml ethanol per 10ml of slurry solution was first added to wet the sample. Injection volume = 25μl

b Samples slurried in a solution containing 10.5g $Mg(NO_3)_2.6H_2O$ per litre of 0.005% Triton X-100 containing 5% (v/v) of ca. 65% HNO_3. Injection volume = 15μl.

3.6.2.2 Sample preparation for beryllium determinations

An appropriate mass of the sample (approximately 0.01 to 0.03g of coal and 0.02 to 0.06g of fly ash) was transferred to a 15ml glass vial containing a magnetic stirrer bar. 15ml of the matrix modifier solution was added. The slurry was sonicated for 5 minutes. For the fly ash determinations, a 1ml aliquot was further diluted to 15ml with the modifier solution. The vial was placed on the modified sample tray of the autosampler. 15μl of the slurry was injected with the autosampler.

3.6.2.3 Procedure

The following analytical procedure was adopted: a minimum of three standard aqueous solutions or standard slurry solutions were used for the construction of a calibration graph. Peak area measurements were recorded and corrected for the blank absorbance. The average of the absorbances of five sample injections was used to determine the analyte concentration. The standard solution or standard slurry was injected after approximately four sample determinations to ensure constant response. Re-calibration was performed when necessary.

Use of platform atomisation necessitated the insertion of an extra "cooling-down" step to allow the platform to return to room temperature. Omission of the extra step, especially with the use of the autosampler, resulted in sputtering of the subsequent sample aliquot due to rapid heating.

3.7 DISCUSSION

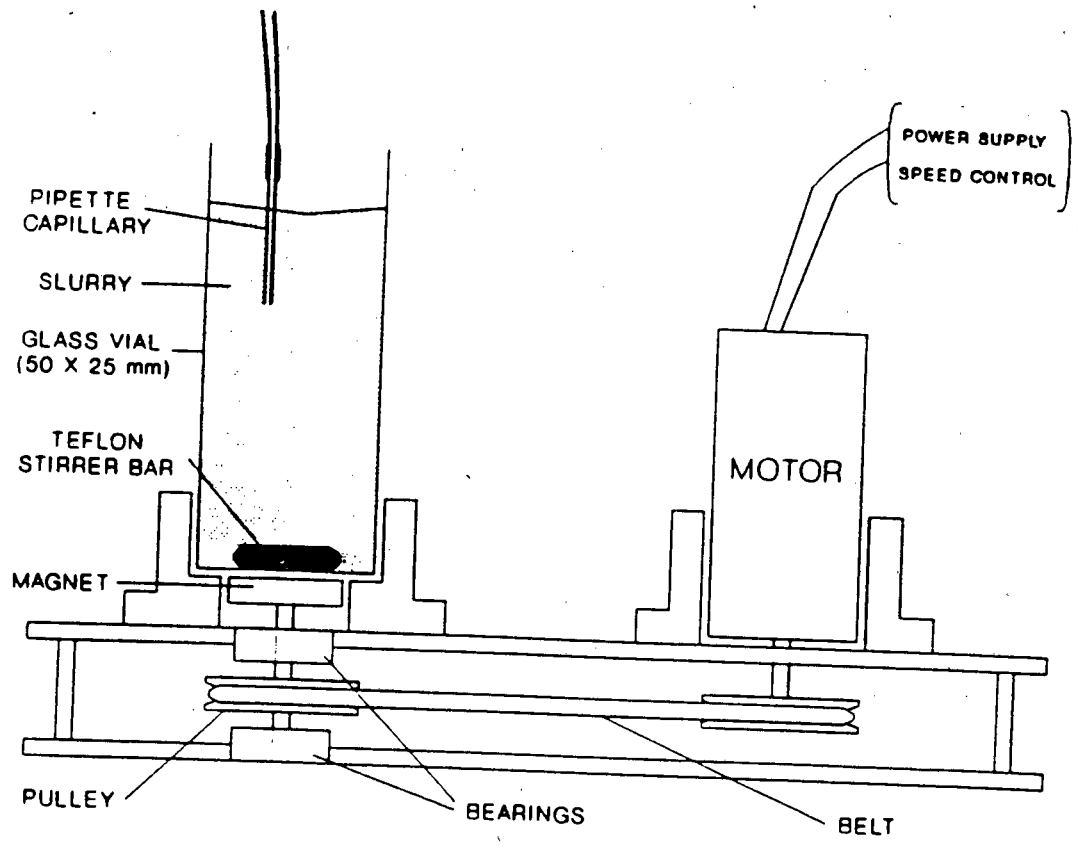
Various aspects of the sample preparation and analytical procedures are applicable to both the cadmium and beryllium determinations. These are discussed below.

3.7.1 Design and operation of autosamplers

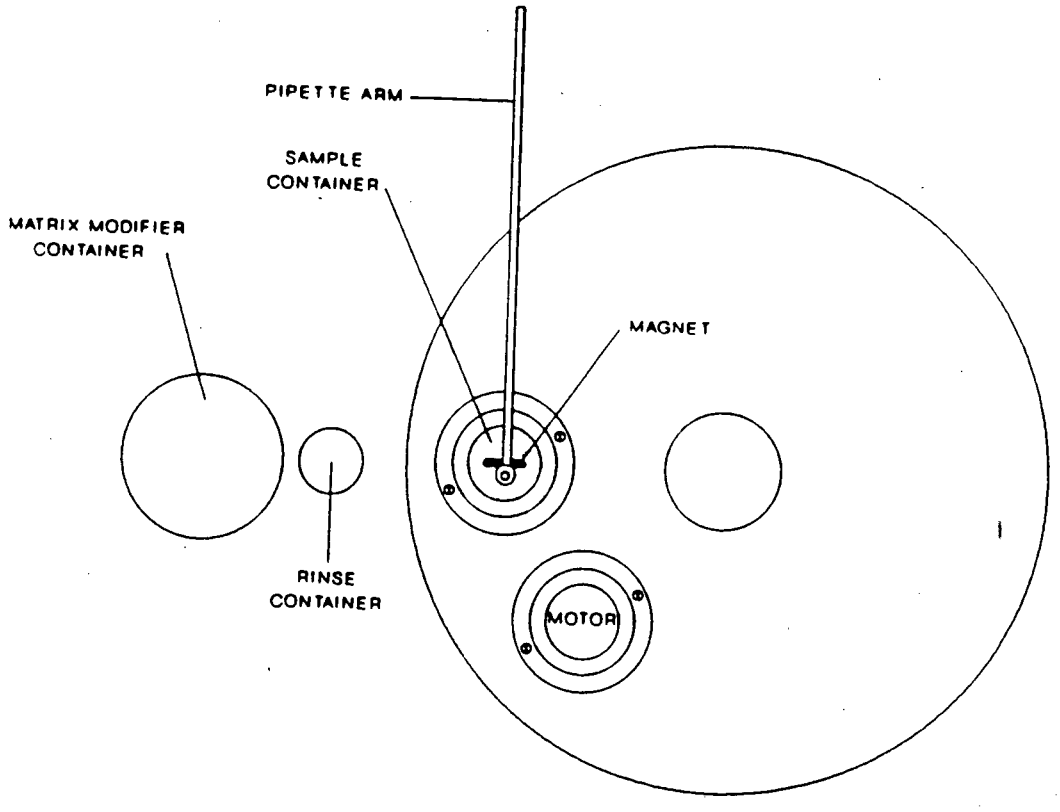
3.7.1.1 Semi automatic autosampler

The AS-40 sample tray was replaced by the unit illustrated in figure 3.2. The unit contains a magnetic stirrer with a 6V motor, as illustrated in figure 3.2A. The speed control allows for fine adjustments of the stirrer speed. The only modification to the AS-40 which was needed was the replacement of the stop-switch which regulates sampling height. This was necessary as the glass vials used for the slurry analysis are 50mm high compared to a height of 25mm for the standard 2ml sample cups. Switch-over between slurry sampling and liquid sampling is achieved by simply removing the slurry tray unit and the stop-switch. Figure 3.2B shows the relative positions of the sample vessel, the motor, rinse container and matrix modifier container. The sampling arm rest position is higher with the slurry autosampler, thus being higher than the rinse container. Insertion of a shortened 1ml plastic pipette tip into the container effectively acted as a rinsing container. The height of the matrix modifier solution container had to be raised for the same reason.

The operation proceeds as for liquid sampling, ie. the capillary is rinsed, an aliquot of the slurry is removed and deposited in the graphite tube, the sampling arm moves to the home position with the capillary resting in the rinse liquid. If an alternate volume is specified, an aliquot from the matrix modifier container is deposited after a



(A)



(B)

Figure 3.2: Semi-automatic autosampler

second rinse and before the arm returns to the rest position. With the modified sampling unit, only one sample in a fixed position can be sampled. The sample, standard and blank solutions have to be replaced manually.

The autosampler is operated in a fixed sample cup position. The nipple on the modified tray positioned the glass vial in sample cup number 18. The autosampler was first driven to vial 18 before placement of the tray. The AS-40 unit was operated in the "manual" mode. The maximum number of replicate readings (99) was specified on the spectrophotometer to avoid the instrument zeroing on the first set of readings. Correction for the blank solution was performed manually.

3.7.1.2 Automatic autosampler

The AS-40 sample tray was replaced by the unit illustrated in figure 3.3. It is composed of a fixed bottom tray incorporating the magnetic stirring components. These are bearings, pulleys, motor and a belt to turn two PTFE stirrer bars. A top view of the stirring geometry is shown in figure 3.3 (b). Two magnets were necessary, one for each row of sample containers (figure 3.3 (c)). As the sample containers are in the same relative positions on the modified tray as they are on the standard tray, the programmer could be used in the normal way. Sampling can therefore occur from either of the rows, the wheels fitted onto the sampling tray allowing the necessary sideways motion (figure 3.3 (c)). The sample container is therefore positioned over the rotating magnet during sampling by the autosampler unit.

Two modifications to the AS-40 autosampler unit were necessary. To accomodate the elevated height of the sample containers, the stop-switch which regulates the sampling arm

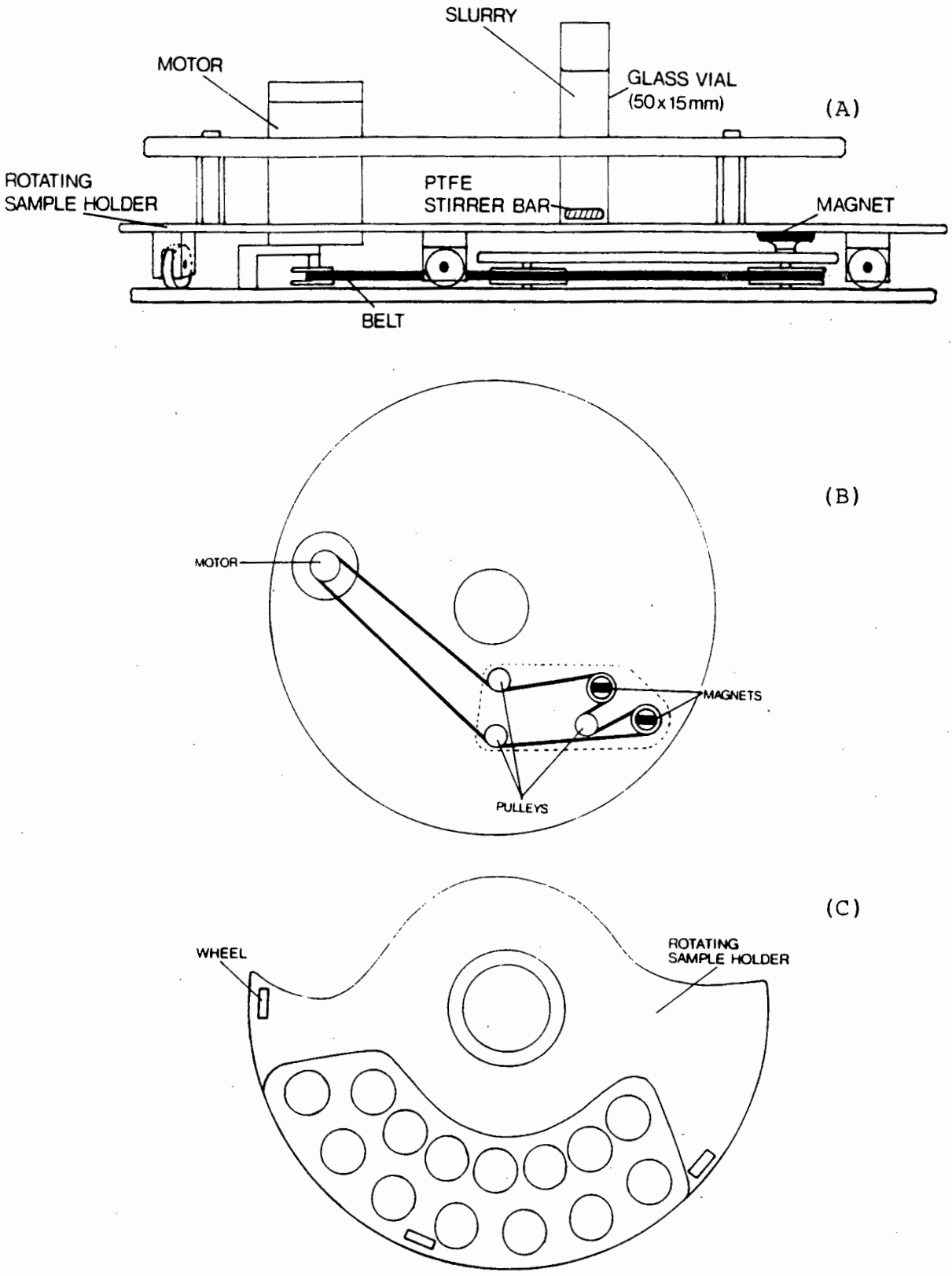


Figure 3.3: Automatic autosampler

had to be removed in the same way as was required for operation of the semi-automatic autosampler tray (section 3.7.1.1). The second modification was the replacement of the standard autosampler arm with a concave arm in order to allow sampling from the inside row. This was necessary as the standard straight arm was obstructed by the sample containers.

The rinsing container and the matrix modifier container were raised to allow for the elevated rest position of the sampling arm.

Due to physical restrictions for movement, a maximum of 14 containers can be accomodated on the modified sample tray. In comparison, the standard liquid tray allows for sampling from all positions on the circular tray. Nevertheless, compared to the semi-automatic unit which requires manual replacement of each sample, unattended sampling from 14 vessels is possible.

In order to use the AS-40 programming unit for unattended analysis, limitations were placed on the geometry of the slurry sample containers. The standard sample cup positions had to be utilised, therefore the largest slurry container which could be used was the 50 x 15mm glass vials illustrated in figure 3.3 (a). The maximum permissable slurry volume is 6ml.

Slurries can be prepared directly in the sample container, or a 6ml aliquot of a slurry solution can be transferred to the container. The procedure followed will depend on the concentration of the element to be determined.

3.7.2 Preparation of slurries

Reagents used in the preparation of slurries have included water [Wil75, Hin85], dilute solutions of Triton X-100 [Ore77, Ore79], dilute solutions of Triton X-100 containing nitric acid [Mil88] and mixtures of organic solvents such as propanol/glycerol [Gil62] and propan-2-ol/water [Stu82]. Slurrying solutions containing matrix modifiers have also been used [Ebd87/3].

Stable gels and suspensions have been prepared with reagents such as starch, gelatin and Viscalex HV 30 [Ful77].

When samples are introduced as slurries some form of agitation is necessary to ensure the maintenance of a homogenous slurry during sampling. The most common form of agitation has been magnetic stirrers [Wil75, Ore77, Hin85] but ultrasonic agitation has also been used [Mil88].

The following criteria were used for the choice of a suitable solvent:

(i) Should not introduce contaminants or adversely affect the analytical procedure
(ii) Relatively inexpensive
(iii) Give stable slurries
(iv) Not foam extensively
(v) Not be too viscous
(vi) Be well tolerated by the equipment

A solution of 0.005% (m/v) Triton X-100 was found to meet the above criteria. The dilute concentrations necessary were cost-effective and low blanks were obtained. No foaming occurred and it was well tolerated by the instrument.

Due to the low levels of cadmium in the coal samples, highly concentrated (3 to 10% (m/v)) slurries were necessary to obtain an absorption signal. In the preliminary work, the concentration of Triton X-100 was increased to 0.04% (m/v) to effectively wet and disperse the hydrophobic coal. Poor atomisation reproducibility was experienced with the resulting slurries.

Several approaches were taken to solve the problem. Further sample grinding and increased sonication time had no effect, indicating that the presence of large particles, poor homogeneity or particle aggregation were not the cause of the irreproducibility. Optimisation of the furnace program did not solve the problem.

The reproducibility of coal slurries prepared in different solvents was investigated (table 3.3). The best precision was obtained with water (2.7 %RSD), 0.04% Triton X-100 giving the worst precision (57.0 %RSD). Water was not suitable for quantitative work as coal particles tended to creep up the sides of the sample container.

Table 3.3: Atomisation precision of PF 87 (ca. 3.5% m/v) slurried in different media

Medium:	Water	0.005% Triton X-100	0.04% Triton X-100	0.04% Propan-2-ol
%RSD	2.7	3.1	57.0	19.9
n	6	7	10	6

The physical process occurring in the tube was studied to explain the differences in the precision observed with the various solvents. Aliquots of the slurries were deposited on the internal surface of a tube which had been cut lengthwise. Excessive spreading of the 0.04% Triton X-100 slurry towards the ends of the tube was observed, whereas the droplets of the other slurries retained the droplet

shape. The poor precision obtained with 0.04% Triton X-100 was attributed to spreading of the sample towards the cooler ends of the graphite tube. The same effect was not observed for fly ash in 0.04% Triton X-100 or for droplets of 0.04% Triton X-100. The effect appears to be due to the combination of the organic coal and the Triton X-100.

To effectively disperse the coal for cadmium determinations, a small quantity of ethanol was first added prior to the addition of the 0.005% Triton X-100 solution. Slurries prepared in this way gave acceptable precision. Omission of the ethanol led to particle aggregation, which could be dispersed by lengthy sonication (approximately 30 minutes depending on the coal sample).

Utilisation of the unmodified AS-40 autosampler for the injection of fly ash suspensions was investigated in an attempt to automate the procedure. A suspension in 1:1 glycerol:propanol solution was found to be stable, but carry-over on the outside of the autosampler capillary impaired the injection precision. Manually wiping the capillary prior to injection improved the situation, but was not conducive to achieving automation. More dilute glycerol mixtures were prepared, but settling of particles was noted. Furthermore, increased ashing times were necessary to remove the glycérol to prevent background interferences during atomisation. It was felt that injection of stable suspensions to achieve automation was not promïsing and further investigations were not made.

3.7.3 **Particle size and grinding procedures**

Sampling error depends on the following factors [Lan85]:

(i) the distribution pattern of the analyte
(ii) the particle size
(iv) the sample amount
(v) the concentration of the analyte

Reduction of the sample particle size is necessary to reduce sampling errors, particularly with inhomogenous samples such as coal and fly ash. Even with unfavourable distribution patterns, the sampling error can be reduced to an acceptable level when the particle size is sufficiently reduced [Lan85]. It is particularly important in the direct analysis of solids as the mass of sample taken is generally less than for digestion procedures.

The certified values for trace elements in NBS SRM coals and fly ashes are for a minimum sample size of 250mg. In trace element analysis using the slurrying method, the mass of each injection lies in the range of 1 to 25μg.

Sample particle size has practical implications as large particles tend to block the tip of the automatic pipette and the capillary tube of the autosampler.

Particle size also affects atomisation efficiency. Hinds et al. [Hin85] determined Pb and Cd in soil and found that with particles greater than 20μm atomisation efficiency was reduced. Fuller [Ful81] observed that particle size effects become significant above 25μm when sampling was the main source of error.

The grinding procedure used to reduce particle size should not contaminate or heat the sample excessively. Excessive

heating increases the possibility of volatile element loss and promotes caking, especially with coal samples. The caking effect is worse for undried samples and interferes with efficient sample grinding. The interrupt control on the Fritsch^{R} allowed for short waiting periods during the grinding procedure to prevent excessive heating. Wet grinding with methanol or ethanol prevents clumping but was not used in this work due to concern about leaching of certain elements during the grinding procedure and the increased risks of contamination.

Table 3.4 (A) illustrates the particle size distribution of a fly ash sample (PFA 9) ground for various times in the ball mill. Most of the size reduction occurred between 10 minutes and 1 hour grinding. The portion ground for 3 hours shows a similar distribution to the portion ground for 1 hour, but was found to have a greater proportion of particles smaller than 20μm. A grinding time of 2 hours was chosen as a compromise.

O'Reilly and Hicks [Ore79] found swing mills to be far superior to any of the other devices they investigated. The use of a Siebteknik swing mill was therefore investigated. A fly ash sample (PFA 58) was ground for 20 minutes in the swing mill and a second portion for 2 hours in the ball mill. The particle size analysis of the portions are illustrated in figure 3.4 (B). The particle size distribution indicates that the swing mill is more efficient, resulting in a greater proportion of smaller particles in a shorter time. However, the swing mill had several disadvantages:

(i) Excessive sample heating
(ii) Lengthy and tedious cleaning procedures necessary to avoid contamination

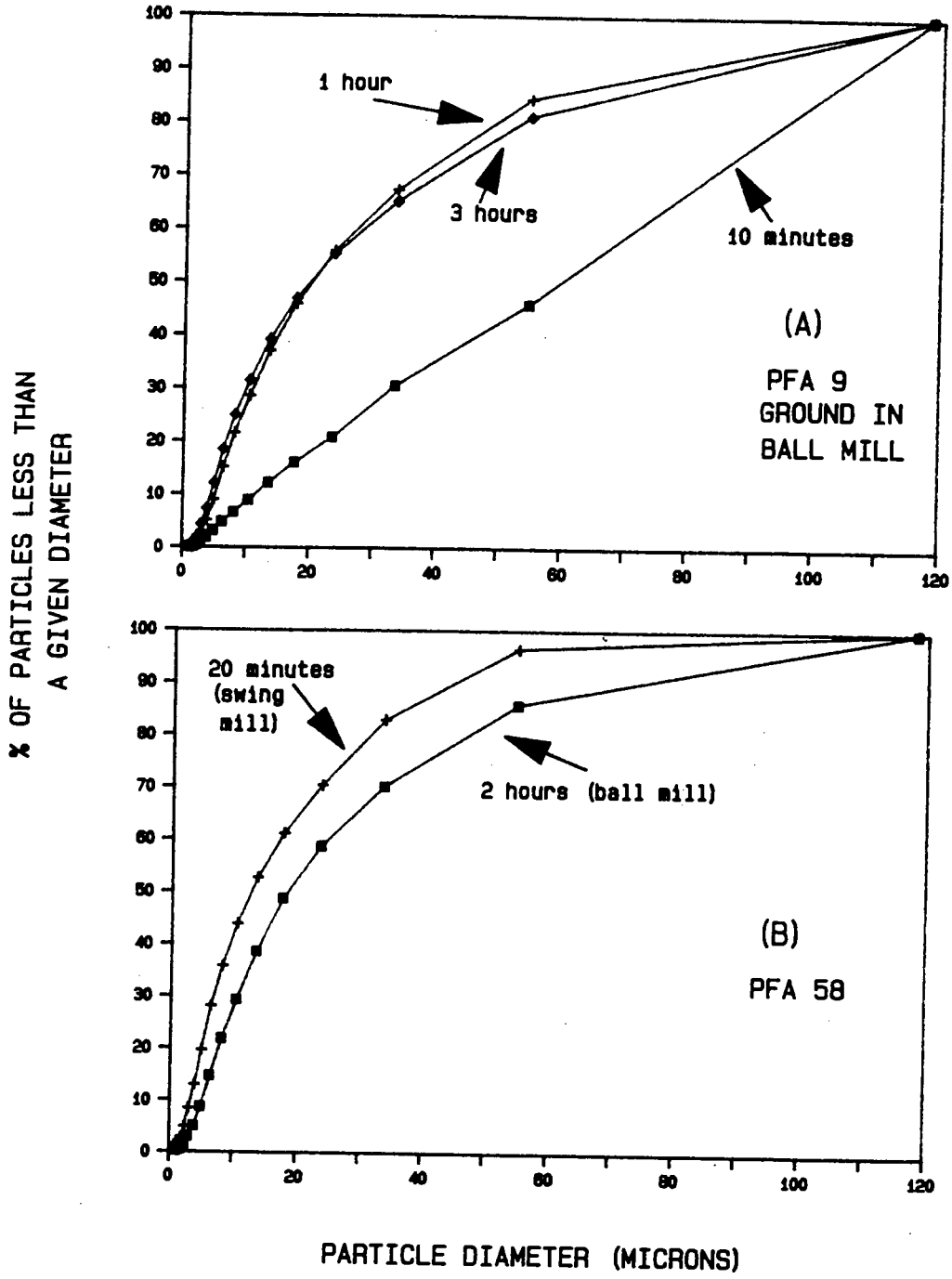


Figure 3.4: Particle size analysis of PFA 9 and PFA 58

(iii) Large samples needed, typically at least 10g
(iv) Very noisy!

Even though the ball-mill was found to be less efficient, it was felt to be more suitable for this work as limited sample masses were available. This is not usually the case and if large samples are available the swing mill may be preferred for size reduction. The particle size analysis of two fly ash samples (PFA 4 and PFA 22) and five coal samples (PF 90, PF 96, PF 99, PF 101 and PF 103) are illustrated in figures 3.5 and 3.6 respectively. The fly ash samples were found to have a greater proportion of smaller particles than the coal samples. The precision of cadmium and beryllium determinations were generally worse in coal samples relative to fly ash samples (chapters 4 and 5) probably as a result of the particle size difference. Figure 3.6 (A) illustrates the variation in particle size distributions obtained with different coal samples. This is dependent on the physical properties of the coal such as plasticity, grindability and hardness of the particular minerals and macerals present [Ore79].

No problems were experienced with poor peak shapes or injection precision. The worst precision was of the order of about 30%, which was felt to be adequate considering the actual sample mass injected.

The effect of particle size on the absorbance peaks of cadmium in PFA 9 is illustrated in figure 3.7. Decreasing the particle size (figure 3.4 (B)) results in peaks which are sharper and more reproducible. The absorbance peaks for an aqueous cadmium standard solution are included for comparison.

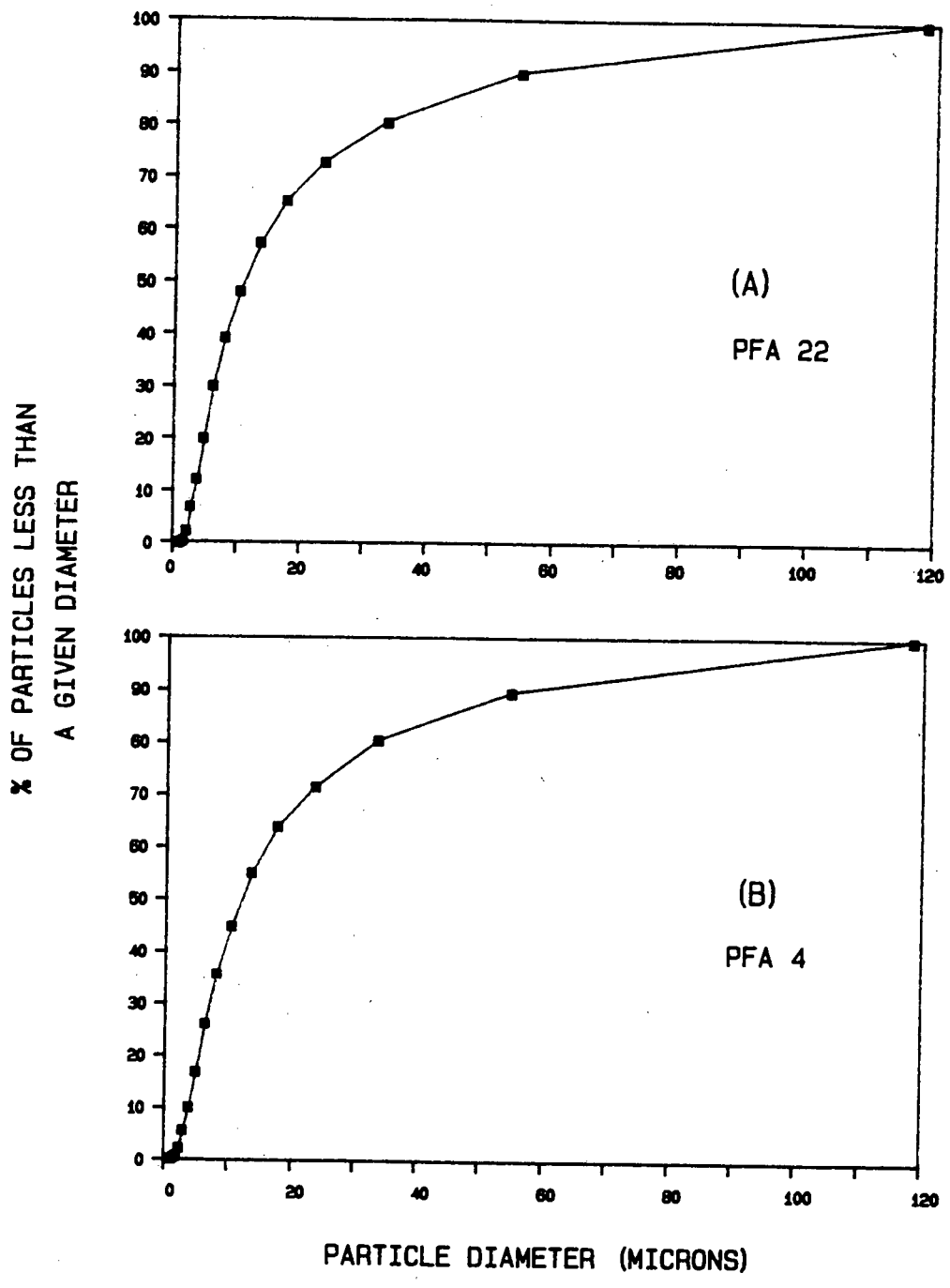


Figure 3.5: Particle size analysis of PFA 22 and PFA 4

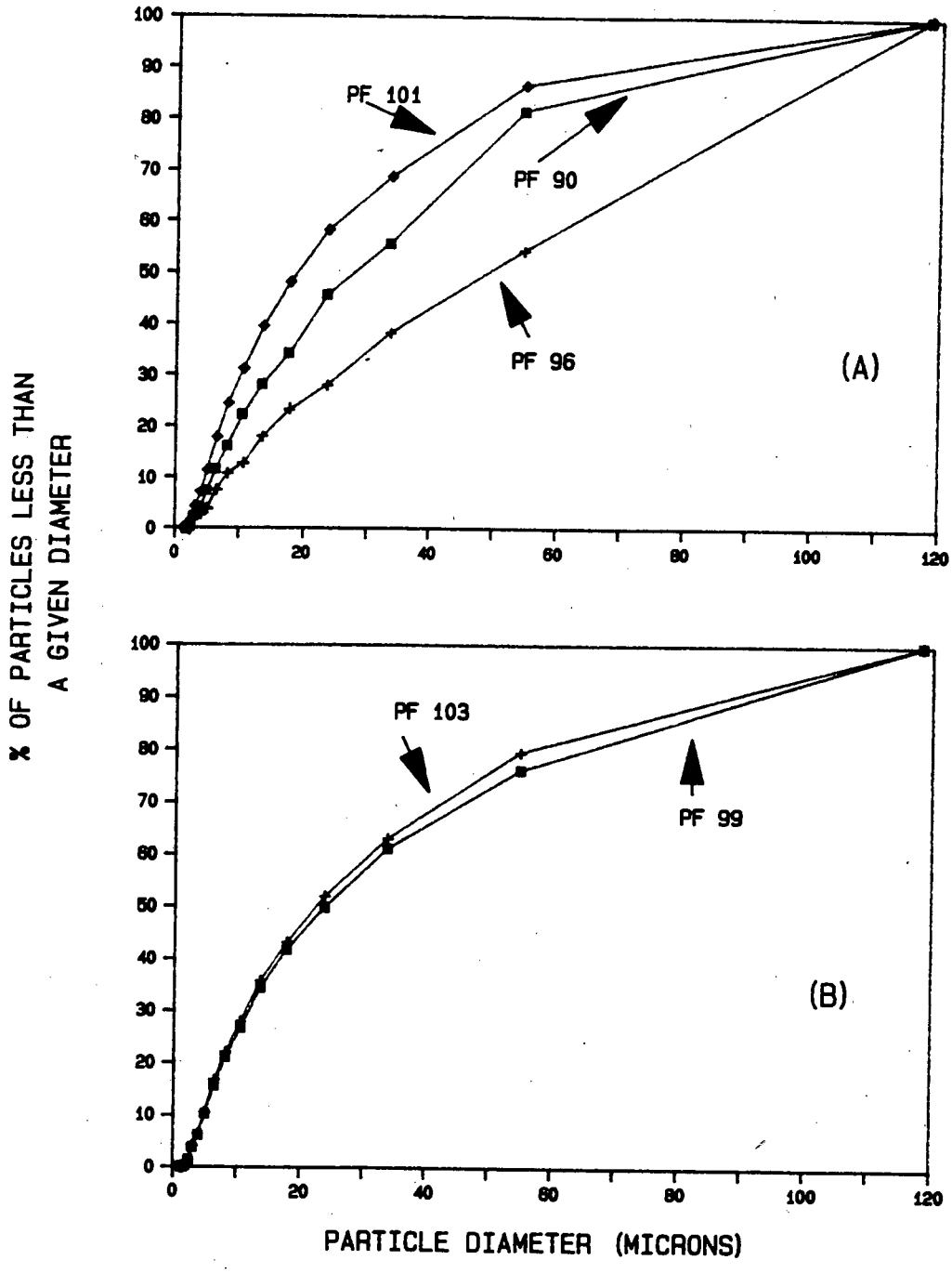
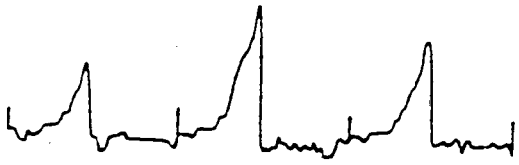
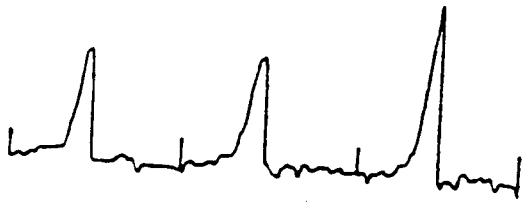


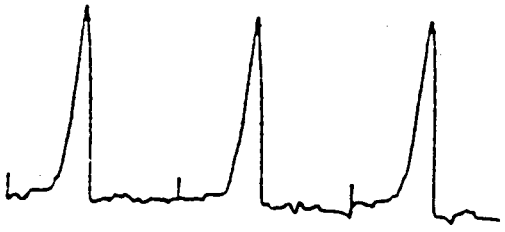
Figure 3.6: Particle size analysis of coals



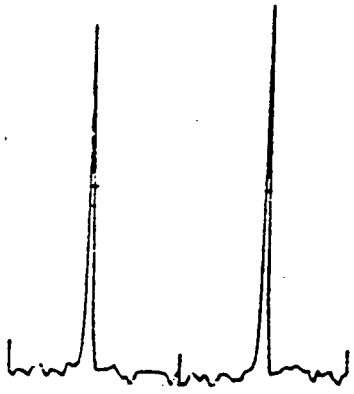
PFA 9: 2.72mg
Ground for 10 minutes



PFA 9: 1.72mg
Ground for 1 hour



PFA 9: 2.28mg
Ground for 3 hours



Aqueous standard
(0.016ng Cd)

All in 0.005% (m/v) Triton X-100

Figure 3.7: Effect of grinding time on cadmium absorbance peaks (228.8nm)

3.7.4 Calibration standards and absorbance measurements

The following calibration methods may be used:

(i) measurement against solid standards (natural or synthetic)
(ii) measurement against aqueous standards
(iii) the standard addition technique using aqueous or solid standards

For simple materials, synthetic solid standards can be made, but this in not generally applicable to most samples, especially complex samples such as coal and fly ash. In these cases, standard reference materials may be more suitable. The expense of these materials may preclude their use on a routine basis, but they may be used to characterise in-house reference standards.

Measurement against aqueous standards is the simplest and cheapest method and has been applied to the analysis of a wide variety of samples. Miller-Ihli [Mil88] determined a number of elements in several NBS reference materials: citrus leaves, coal, pine needles, wheat flour, bovine liver, orchard leaves, rice flour, tomato leaves and spinach leaves. Good agreement with certified values were obtained, with integrated peak area measurement giving more accurate and precise results than peak height measurements. Schlemmer and Welz [Sch87] determined cadmium and nickel in coal, coal fly ash and urban particulate matter reference standards. Calibration against aqueous standards gave good agreement with the certified values for the cadmium determinations, but slightly lower results were obtained for nickel. The authors recommend the use of solid reference standards for nickel determinations. Ebdon and Lechotychki [Ebd87] determined cadmium in environmental samples using

aqueous calibration, good agreement with certified values were obtained.

3.8 CONCLUSION

The equipment and experimental procedures used for the direct determination of cadmium and beryllium in coal and fly ash slurries were outlined. Various aspects of the experimental procedures which are applicable to both the cadmium and beryllium determinations, as well as to other direct solid analysis procedures, were discussed.

4

DETERMINATION OF CADMIUM IN COAL AND FLY ASH

4.1 INTRODUCTION

The detection limits of the most important methods for cadmium determinations (table 4.1, reproduced from Sto86), indicate that GFAAS is one of the most sensitive techniques.

Table 4.1: The detection limit is defined as three times the Standard Deviation (S.D.) of noise or blank in non-interfering analyte solution (Neutron activation analysis (NAA): non-interfering matrix). Values given in µg/l (µg/kg for NAA).

Method	Detection limit
Voltammetry (film electrode)	<0.0002
AAS, graphite furnace[a]	≤0.003
Total reflection XRF[a]	0.4
Neutron activation analysis[b]	≤1.5
ICP-AES	<3
AAS with flame (Zeeman background correction)	3

[a]Usually a 50µl sample volume is considered; if higher sample volumes can be taken, the D.L. is lower.
[b]Sophisticated radiochemical separation procedures attain detection limits well below 1µg/kg.

However, the high volatility of cadmium can make its determination by GFAAS problematic [Bau85]. In volatile matrices, where little difference exists between the volatility of the matrix and the analyte, effective removal of the matrix constituents may result in analyte losses. Incomplete removal of the matrix components leads to background interference during atomisation, which may not be adequately corrected by the background correction system.

If the matrix is refractory, selective volatilisation can be used to separate the matrix from the analyte peak [Bau85]. This allows atomisation to occur before the matrix background peak appears.

Coal is relatively volatile due to the high concentration of organic components present. Fly ash is a refractory matrix

consisting predominantly of fused aluminosilicates and small quantities of unburnt coal [Fis78]. The chemical components of several South African coals and fly ashes appear in table 4.2.

Table 4.2: Chemical components of selected South African coal and fly ash samples [Wil82]

	Concentration (%)					
Constituent	PF 87 AR4 PF	PF 89 CA6 PF	PF 101 MA1 PF	PFA 4 AR4 LH2	PFA 13 CA6 LH2	PFA 48 MA1 LH4
SiO_2	11.4	8.6	11.4	53	51	39
TiO_2	0.45	0.28	0.45	1.5	1.3	1.6
Al_2O_3	7.3	3.9	7.3	27	22	27
Fe_2O_3				4.8	7.2	4.7
FeO	0.75	0.97	0.75			
MnO	0.01	0.01	0.01	0.05	0.02	0.05
MgO	0.67	0.43	0.66	2.0	2.1	3.2
CaO	2.5	1.9	2.5	6.7	8.6	13
Na_2O	0.10	0.10	0.11	0.21	0.65	0.94
K_2O	0.19	0.11	0.19	0.51	0.65	0.93
P_2O_5	0.26	0.14	0.26	0.89	1.1	2.2
S	0.82	0.90	0.81	0.34	0.64	0.73
Organic matter	75.6	82.7	75.6	2.2	4.9	6.5

Chemical treatment has been used to eliminate some of the problems experienced when the analyte and matrix volatilities are similar [Mat81]. "Matrix modifiers" [Edi75] are used to chemically stabilise the analyte. Higher ashing temperatures can be employed, thus facilitating matrix volatilisation without simultaneous analyte loss. Ammonium phosphate salts [Sch87], mixtures of ammonium phosphate/magnesium nitrate [Bet86] and palladium nitrate/ammonium nitrate [Yin87] have been used for the prevention of cadmium ashing losses. Baucells et al. [Bau85] determined cadmium in soil extracts with a $HNO_3/Mo/H_2O_2$ analyte modifier. They also investigated $NH_4H_2PO_4$ modifier and found that the peak height of the sample was low when charred below 400°C, whereas the peak area remained constant. This was attributed to the

appearance of two peaks. Similar profiles were found with H_3PO_4, H_2SO_4 and $(NH_4)_2SO_4$. Bettinelli et al. [Bet88] determined cadmium in digested fly ash samples. An ashing temperature of 1000°C was possible with a $Pd/Mg(NO_3)_2$/glycerol modifier.

The introduction of oxygen has been used to facilitate ashing of intact organic matrices. Oxygen also inhibits the build-up of carbonaceous residues in the tube which occurs in an inert ashing atmosphere [Bea80, Gro82, Ste85, Sch87]. In the absence of oxygen, the process taking place in the furnace is pyrolysis rather than true ashing and the enclosed Massmann-type furnaces can benefit from the addition of oxygen into the purge gas during ashing [Mat81].

Oxygen ashing has successfully been applied to the analysis of a wide range of organic/biological samples. Beaty et al. [Bea80] examined the effectiveness of oxygen in reducing matrix interferences in the analysis of serum samples. They investigated the influence of oxygen ashing on the sensitivity of several elements using both standard and pyrolytically-coated tubes. For cadmium, no change in sensitivity was noted, but an increase in sensitivity was found for lead, zinc and indium. Eaton and Holcombe [Eat83] studied the effects of nitric acid, ammonium phosphate, air ashing and Triton X-100 on the determination of lead in blood using GFAAS. Air ashing (about 20% oxygen) resulted in more complete removal of the organic-based matrix. Ammonium phosphate salts gave a higher background after air ashing than in the absence of phosphate salts. The authors suggest that the efficiency of the air ash is reduced in the presence of phosphate salts. Narres et al. [Nar84] used oxygen ashing for the determination of Cd in oil. Temperatures exceeding 500°C could be used without ashing losses. Schlemmer and Welz [Sch87] determined cadmium and nickel in powdered coal, fly ash and urban particulate

matter reference standards. For the cadmium determinations, the sample was soaked with a matrix modifier solution containing $NH_4H_2PO_4/HNO_3$/Triton X-100. Oxygen ashing eliminated the background originating in the coal matrix but was not advantageous for the fly ash or urban particulate matter samples.

Several researchers [Eat 83, Nar 84] have reported on the analyte modifying effect of oxygen, thus permitting higher ashing temperatures to facilitate matrix removal. Salmon and Holcombe [Sal82] proposed a mechanism to explain the shift to the higher appearance temperatures observed for Pb, Cd, Zn and Ag in the presence of oxygen. The hypothesis is based on the assumption that the production of gas phase atoms can be expressed by the following equation:

$$MO(s,l) + C \longrightarrow M(g) + CO(s)$$

The existence of two types of active sites on the graphite surface with different activation energies for metal oxide reduction was proposed. Oxygen reacts with type I active sites (low activation energy) with the type II sites (higher activation energy) being available for reduction of the metal oxide. This results in a shift to higher appearance temperatures.

Stoeppler [Sto86] reviewed the methodological progress in cadmium analysis in biological and environmental materials. The remarkable progress achieved in GFAAS is attributed to the use of pyrolytically coated graphite tubes and more flexible furnace systems thus allowing variable temperature ramping and alternate sheath gases. Effective background correction systems such as Zeeman and Smith-Hieftje and the stabilized temperature platform furnace (STPF) methodology (use of L'vov platforms with matrix modification) has led to

peak area rather than peak height determinations, thus yielding more accurate GFAAS data.

This work investigates the determination of a volatile element, Cd, in both a volatile matrix, coal, and a refractory matrix, fly ash. The problems associated with each will be dealt with separately.

4.2 VOLATILITY OF THE COAL AND FLY ASH MATRIX

The appearance temperatures of the coal and fly ash matrix components were investigated. An aliquot of a coal or fly ash slurry was injected into the tube and dried. The temperature was then raised from 100°C to 2700°C in 120 seconds and the background absorbance monitored for the Cd 228.8 nm line. The recorder traces for PF 88 (335μg) and PFA 48 (480μg) are reproduced in figure 4.1.

The fly ash matrix is volatilised above 1600°C (figure 4.1 (b)), thus allowing the cadmium atomisation to precede the matrix volatilisation.

The bulk of the coal matrix is volatilised before 750°C (figure 4.1 (a)). As cadmium losses occur at this temperature in the coal matrix, selective volatilisation cannot be used to separate the atomisation peak from the background peak.

A portion of the coal is volatilised above 1600°C. The appearance temperature and relative size of the background signal indicate that the signal is due to the inorganic fraction of the coal.

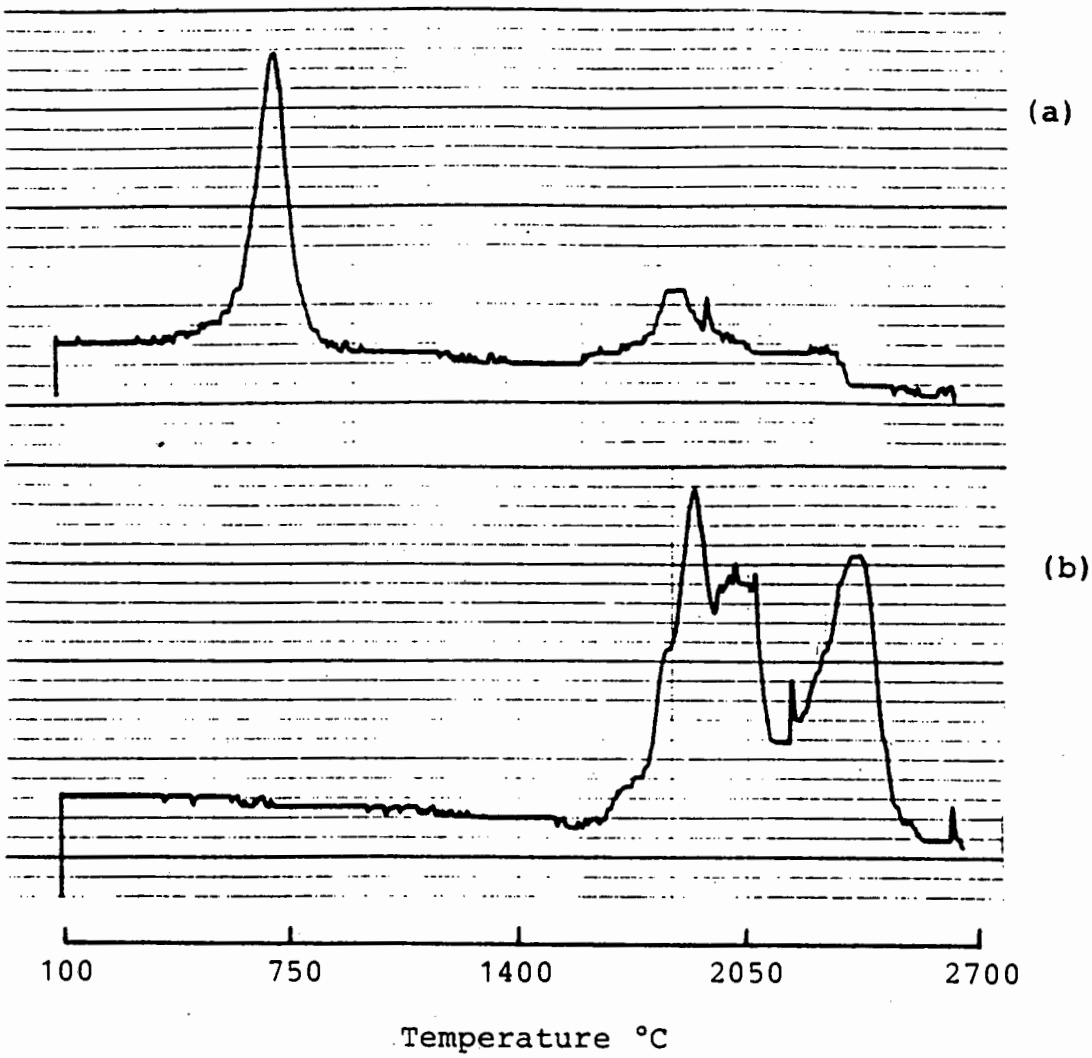


Figure 4.1: Broad band absorption at the cadmium 228.8 nm line
(a) Coal - 335µg PF 88
(b) Fly ash - 480µg PFA 48

Internal gas flow: 300ml argon/minute
Chart speed: 60mm/minute

4.3 DETERMINATION OF CADMIUM IN FLY ASH

4.3.1 Analysis of solid samples

Solid samples were injected with the powder sampler described in section 3.1.

Preliminary investigations were undertaken with NBS SRM 1633a fly ash. The cadmium concentration in this sample is too high (1μg/g) for use of the first detent position on the sampler, corresponding to the minimum mass. The fly ash was diluted by manually grinding a portion with graphite powder in an agate mortar and pestle. The diluted sample was analysed by ashing at 800°C and atomising at 1400°C. Sharp single peaks with no shoulders were obtained. The mass dispensed was obtained by difference and the %RSD (n=10) was found to be 8.6%.

A calibration graph (r=0.9945) constructed by analysing three dilutions of the NBS SRM 1633a was used to determine Cd in PFA 47. A value of 0.10μg/g was obtained, which agrees with the result obtained with the slurry method (see table 4.10).

Successive atomisations of fly ash samples were found to lead to double peaks, a phenomenon which did not occur with the NBS SRM fly ash. Variation of ashing and atomisation temperatures did not improve the situation. The possibility that the single peaks obtained with the NBS sample may be due to the presence of the graphite was investigated. Fifteen successive atomisations of the undiluted NBS sample were performed, with a high internal gas flow (300ml/minute) used to reduce sensitivity. No double peaks were obtained, but differences in the peak widths were noticed.

The effect of addition of various liquid reagents on the atomisation peaks of PFA 48 were investigated. The liquid reagent was injected on top of the powder mound in the tube. The sample was analysed and the absorbance peaks recorded. Dilute solutions of nitric acid, phosphoric acid, Triton X-100 and water all improved the peak shape. A 1% (m/v) solution of Triton X-100 was found to be the most effective. The atomisation peaks in the presence and absence of 1% Triton X-100 are reproduced in figure 4.2.

The improvement was attributed to the wetting effect of the Triton X-100 which leads to sample spreading along the tube. It is hypothesized that the more intimate contact between the sample and tube leads to improved ashing and atomisation. The sample powder mound in the tube experiences a temperature gradient, resulting in inefficient ashing and poor atomisation. Addition of a good conductor of heat, such as graphite, reduces the thermal gradient in the sample mound thus improving ashing and atomisation. It may be possible that the residual organic matter in fly ash samples serves the same purpose, as the extent of double peaks differed for the various fly ash samples investigated.

Eaton and Holcombe [Eat83] found that addition of Triton X-100 reduced the interfacial tension between whole blood samples and the graphite tube thus improving contact between the sample and tube wall. In the absence of Triton X-100 the ashing stage was inefficient. Grobenski et al. [Gro82] studied the analysis of solid biological NBS SRM reference standards. Sample contact with the graphite surface was improved by the addition of 10μl of 0.1% nitric acid on top of the sample in the tube. Kersabiec and Benedetti [Ker87] determined trace elements in geological samples using the solid sampling technique. For all the elements studied, except mercury, it was necessary to dilute the samples with graphite to obtain reliable results. In the absence of

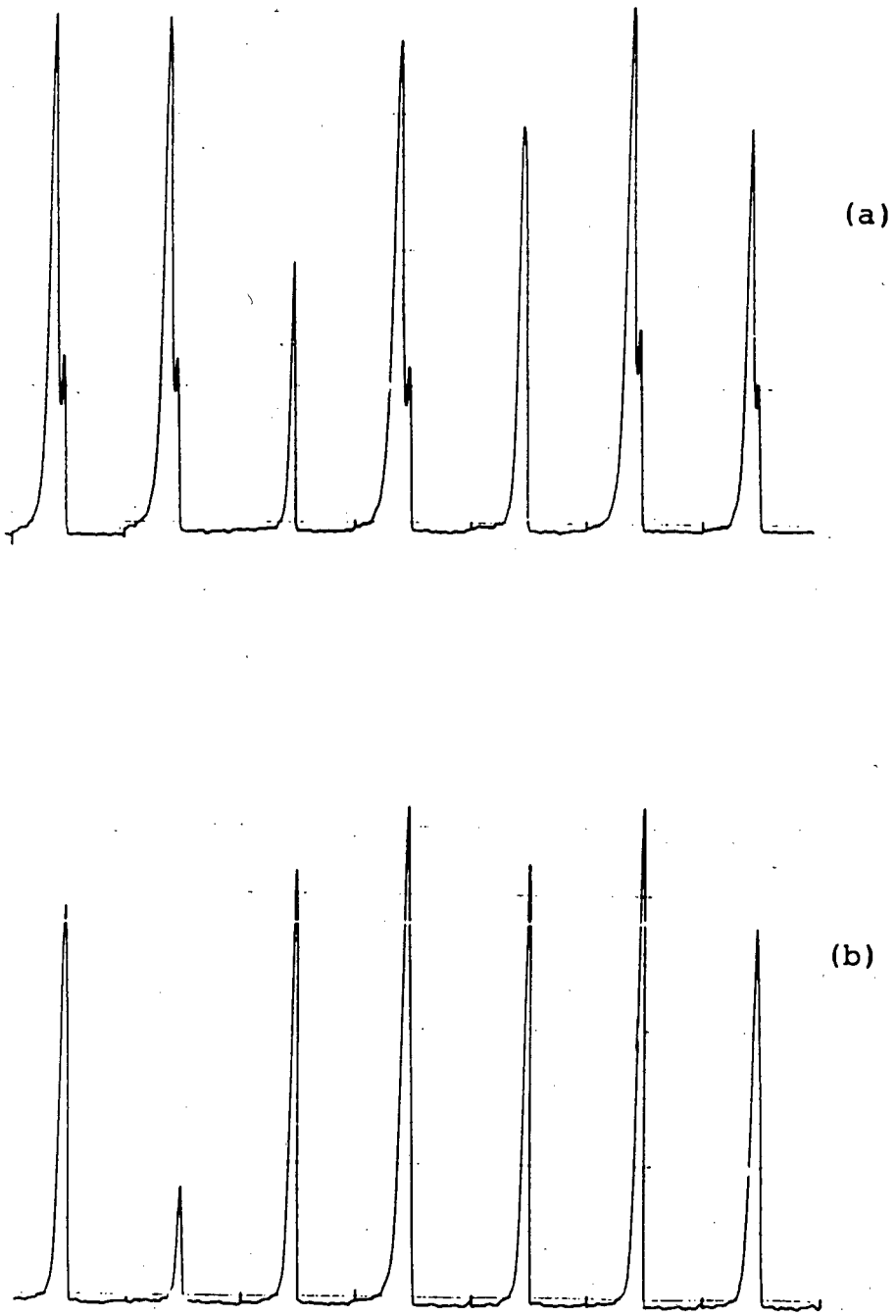


Figure 4.2: Atomisation peaks of PFA 48 (approximately 2mg)
(a) No Triton X-100 added
(b) With 50µl 1% (m/v) Triton X-100

graphite, double peaks were observed. Addition of liquid and solid modifiers on top of the undiluted samples did not give usable peaks. It is possible that the problems these authors experienced ~~is~~ was a result of poor sample/tube contact.

The flow properties of the fly ash may be important for successful analysis, a good flow leading to better spreading of the sample in the tube. Older tubes were found to give more problems with double peaks, probably due to the graphite surface becoming more pitted, thus inhibiting flow.

The direct analysis of the powder samples had two main disadvantages over the slurry method: the need for weighing the powder sampler before and after each injection and for injecting a suitable liquid onto the powder mound to obtain effective ashing and atomisation. It was also noted that during injection of the sample a puff of powder was emitted from the sample introduction hole. The losses occurring in this way are likely to be small compared to the total mass injected, but would compromise the accuracy of the method.

With very low analyte concentrations, the method of powder injection may be preferred over the slurry method, as highly concentrated slurries are necessary to obtain absorption signals. The concentrated slurries are difficult to pipette due to the high mass:volume ratio.

Direct powder analysis is useful when limited sample masses are available or for analyte homogeneity investigations.

All further work was done with injection of slurried samples.

4.3.2 Analysis of slurry samples

The atomisation and ashing curves (Appendix II) for cadmium in NBS SRM 1633a, PFA 48 and an aqueous standard appear in figure 4.3 (a), (b) and (c) respectively.

Cadmium losses occur above 1000°C in both fly ashes, figure 4.3 (a) and (b). Volatilisation losses from aqueous solution occurs above 300°C, figure 4.3 (c). Cadmium stabilisation occurs in the fly ash matrix, illustrating that volatility is not an intrinsic property, but is dependent on the matrix composition [Fre77].

At ashing temperatures above 500°C, an increase in peak heights were observed for both fly ash samples. A similar effect was not observed in the peak area measurements. Figure 4.4 illustrates the atomisation peaks for NBS SRM 1633a and PFA 58 at ashing temperatures of 200°C and 600°C. At 600°C, the peaks are higher and sharper than those obtained at 200°C. Slight shoulders are evident at the front of the peaks obtained at 200°C. Sample particle size also had an influence. Decreasing the particle size reduced the relative difference between the peak heights at the two ashing temperatures.

Due to the differences in ashing behaviour between the fly ash slurries and the aqueous standards, calibration against aqueous standards requires that low ashing temperatures are used, which yields unsuitable atomisation peaks for the samples.

The background absorption signals for the fly ash samples at different atomisation temperatures appear in figure 4.3 (a) and (b). At atomisation temperatures greater than 1600°C, the background rises sharply but is relatively small at lower temperatures (less than 0.2 absorbance units).

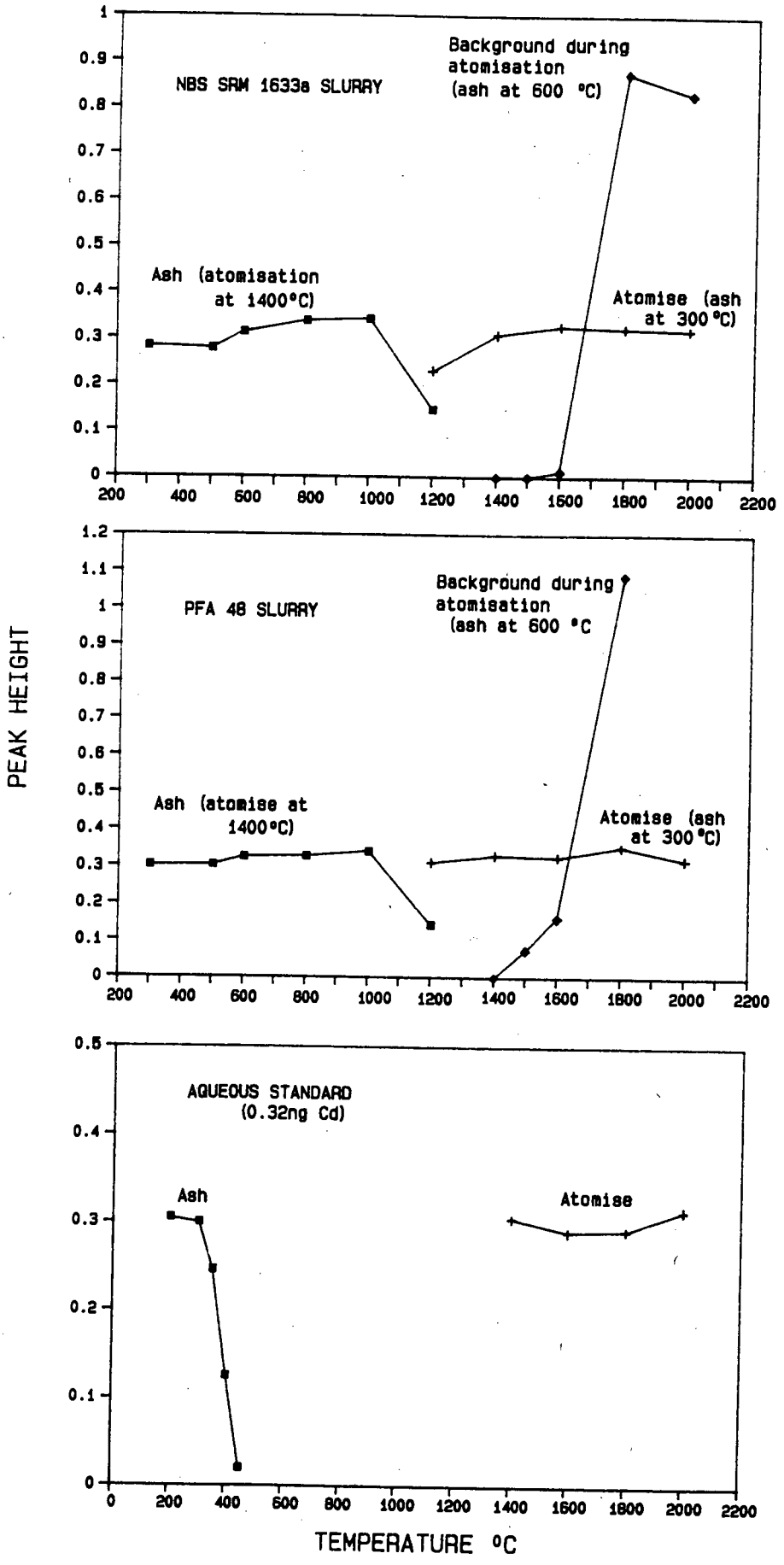


Figure 4.3: Ashing and atomisation curves for
(a) NBS SRM 1633a
(b) PFA 48
(c) Aqueous standard

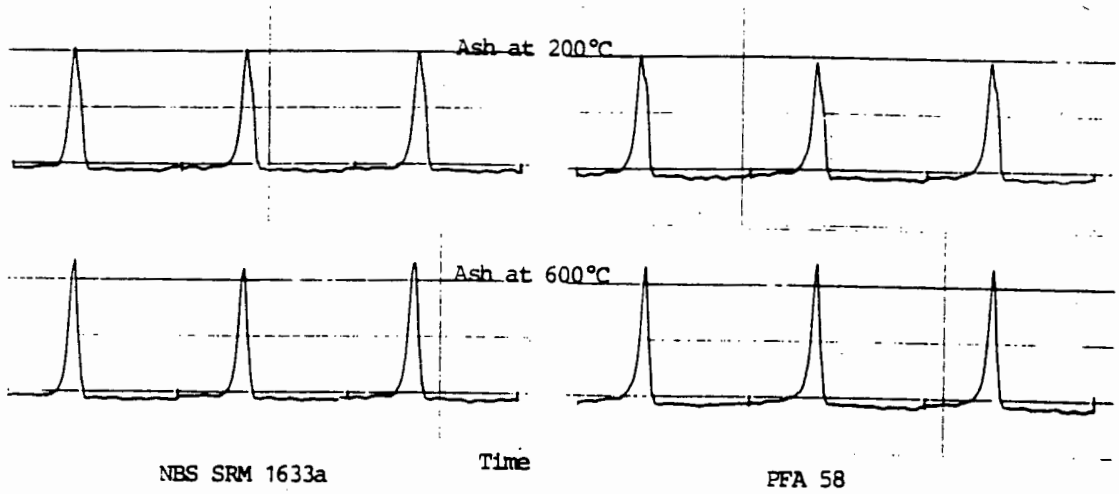


Figure 4.4: Effect of ashing temperature on fly ash peak shapes
Atomisation at 1400°C

The practical implications of a large background signal on the atomisation peak is illustrated in figure 4.5. A fly ash slurry was atomised at 1400°C and 1800°C and the absorbance monitored during the ashing, atomisation and cleaning steps.

Figure 4.5 (a) depicts the background absorption at the two atomisation temperatures. At 1400°C, the background absorbance is small during atomisation, the bulk of the matrix volatilising during the cleaning stage. However, at 1800°C, a substantial portion of the background appears during atomisation.

The uncorrected signal (deuterium arc lamp off) is reproduced in (b). Multiple peaks are obtained at 1800°C, due to both the atomic and background absorbances. A single peak is observed at 1400°C.

The background corrected atomic absorption peaks (deuterium arc lamp on) are illustrated in (c). The negative peak at

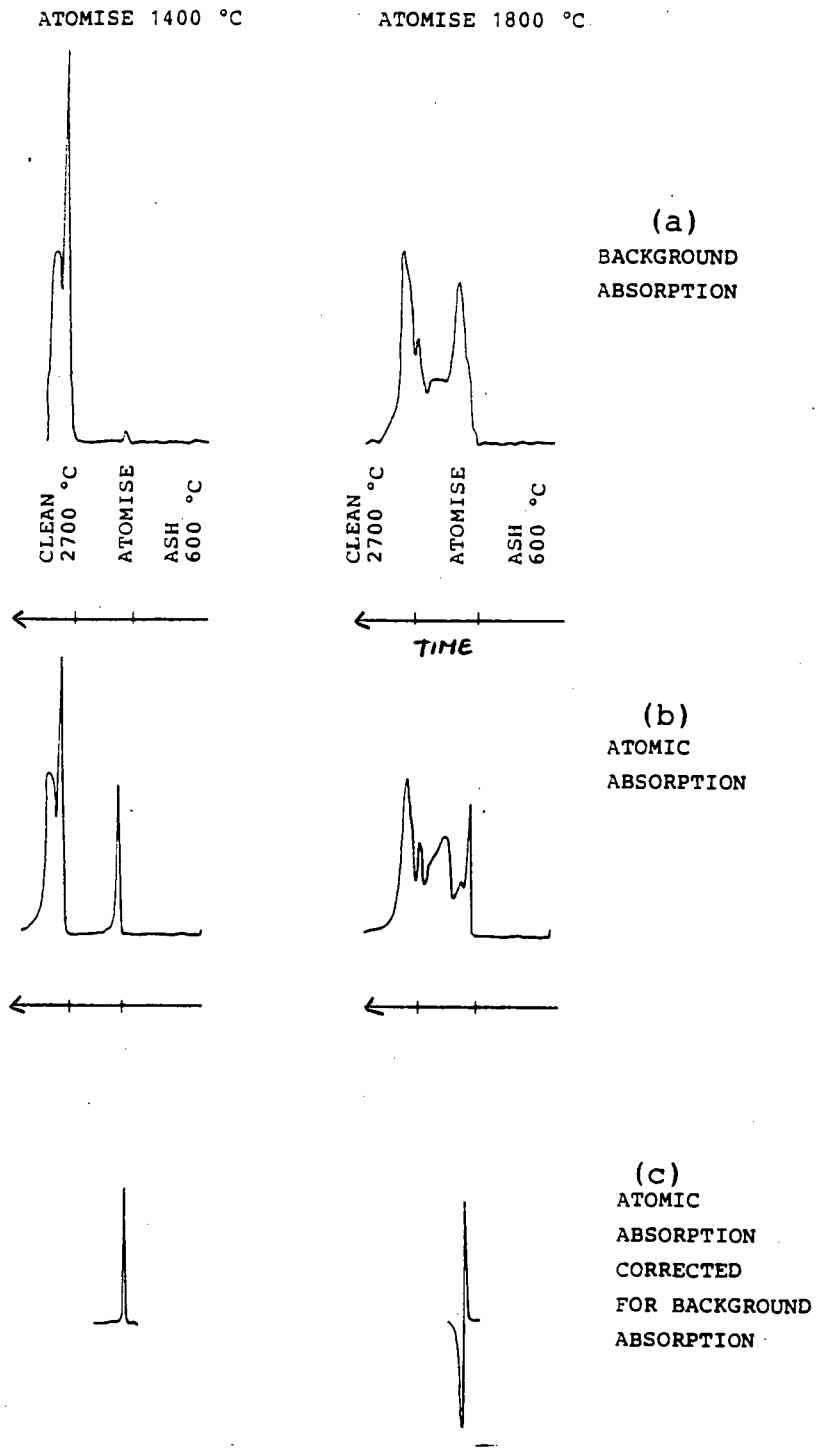


Figure 4.5: Selective volatilisation of cadmium in fly ash matrix

the tail of the 1800°C atomisation peak is due to the momentary reduction in the intensity of the deuterium lamp caused by smoke and/or particulate matter. This peak is unsuitable for quantifications using integrated peak areas, as the absorbance will reflect a summation of the positive and negative peaks. Peak height readings, which are measured at the peak maximum, will remain constant. This is illustrated by the constant peak heights in the atomisation curves in figure 4.3 (a) and (b).

Separation of the cadmium absorbance peak from the background can therefore be achieved by careful selection of atomisation temperature. The determination of cadmium in fly ash, without matrix modification, illustrates the practical application of the concept of selective volatilisation.

The samples were analysed by ashing at 600°C and atomising at 1400°C. Calibration was against NBS SRM 1633a reference slurries.

4.4 DETERMINATION OF CADMIUM IN COAL

The technique of matrix modification was applied to the analysis of coal to overcome the problem of the similar volatilities of the analyte and sample matrix. The suitability of nitric acid, oxygen ashing and ammonium dihydrogen orthophosphate modifier were investigated; each will be dealt with separately. The modifier was also investigated for fly ash determinations in order to develop a single procedure for both coal and fly ash samples.

4.4.1 Use of nitric acid

The effect of nitric acid concentration on the background absorbance of a NBS SRM 1632a slurry in 0.005% Triton X-100

is illustrated in figure 4.6. The curve was obtained by pipetting 50μl of the nitric acid solution into the tube containing the slurry sample aliquot and measuring the background absorbance during atomisation.

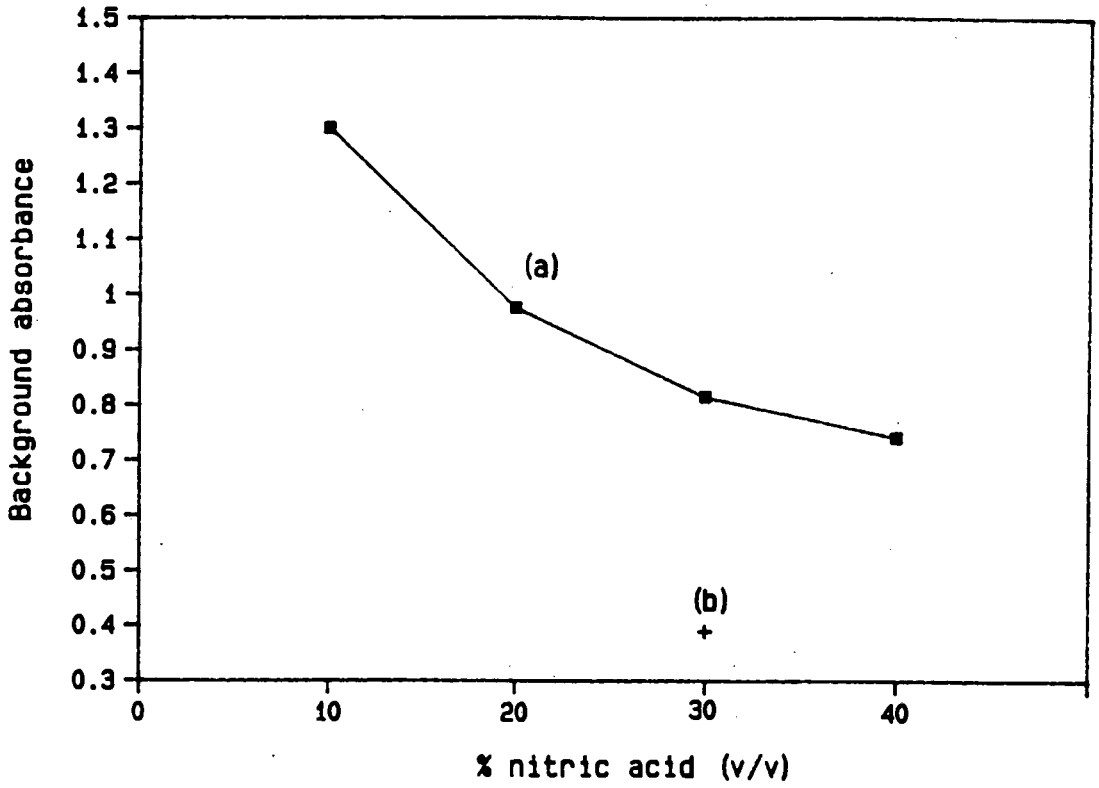


Figure 4.6: Effect of nitric acid concentration on the background absorbance of NBS SRM 1632a slurry

The background absorbance decreased with increasing nitric acid concentration. More efficient ashing was achieved by the preparation of the slurry in a solution of nitric acid

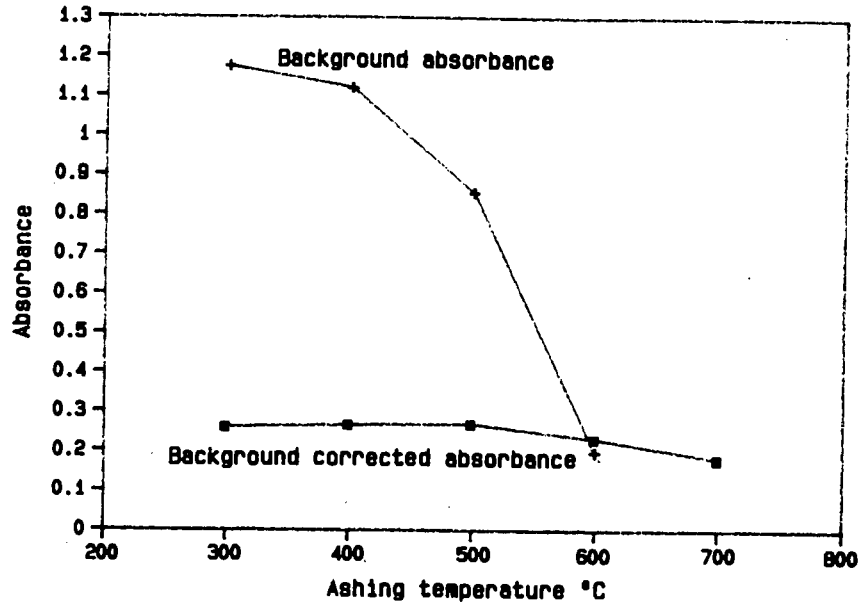
(point (b) on the curve), compared to the addition of the acid solution to the sample in the tube . This is probably a result of improved contact between the sample and the ashing aid (nitric acid).

The ashing profiles of NBS SRM 1632a slurries prepared in 10% and 20% (v/v) of 65% nitric acid appear in figure 4.7. At ashing temperatures below 600°C, the background absorbance in the 20% nitric acid solution is approximately half that obtained in the 10% solution. At 600°C the background absorbances are similar. A small analyte modification effect is obtained; ashing losses occur above 500°C in the 10% nitric acid solution and above 700°C in the 20% solution.

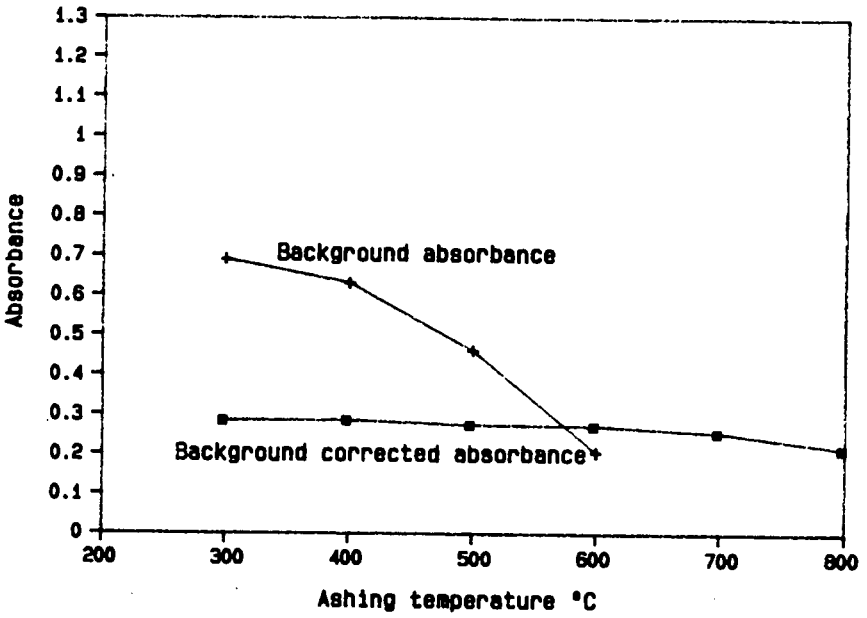
The influence of ashing ramp and hold times are illustrated in figure 4.8. The analytical furnace parameters should reflect a compromise between minimum background absorbance and analysis time.

An attempt was made to analyse coal samples slurried in 20% nitric acid. Several problems were encountered which made the procedure unsuitable for routine application. The build up of carbonaceous residues in the tube, coupled with severe tube degradation due to the high nitric acid concentration, seriously affected the analytical precision. The tube deteriorated rapidly, after about 45 firings the sensitivity had decreased to approximately one third of the original value. Frequent calibration was therefore necessary. Furthermore, high background absorbances were still obtained for certain samples eg. NBS SRM 1635.

The method was felt to be unreliable and costly due to the high replacement cost of the tubes. Further investigations were not undertaken.



(a)



(b)

Figure 4.7: Ashing curves for NBS SRM 1632a in the presence of nitric acid
(a) 10% nitric acid
(b) 20% nitric acid

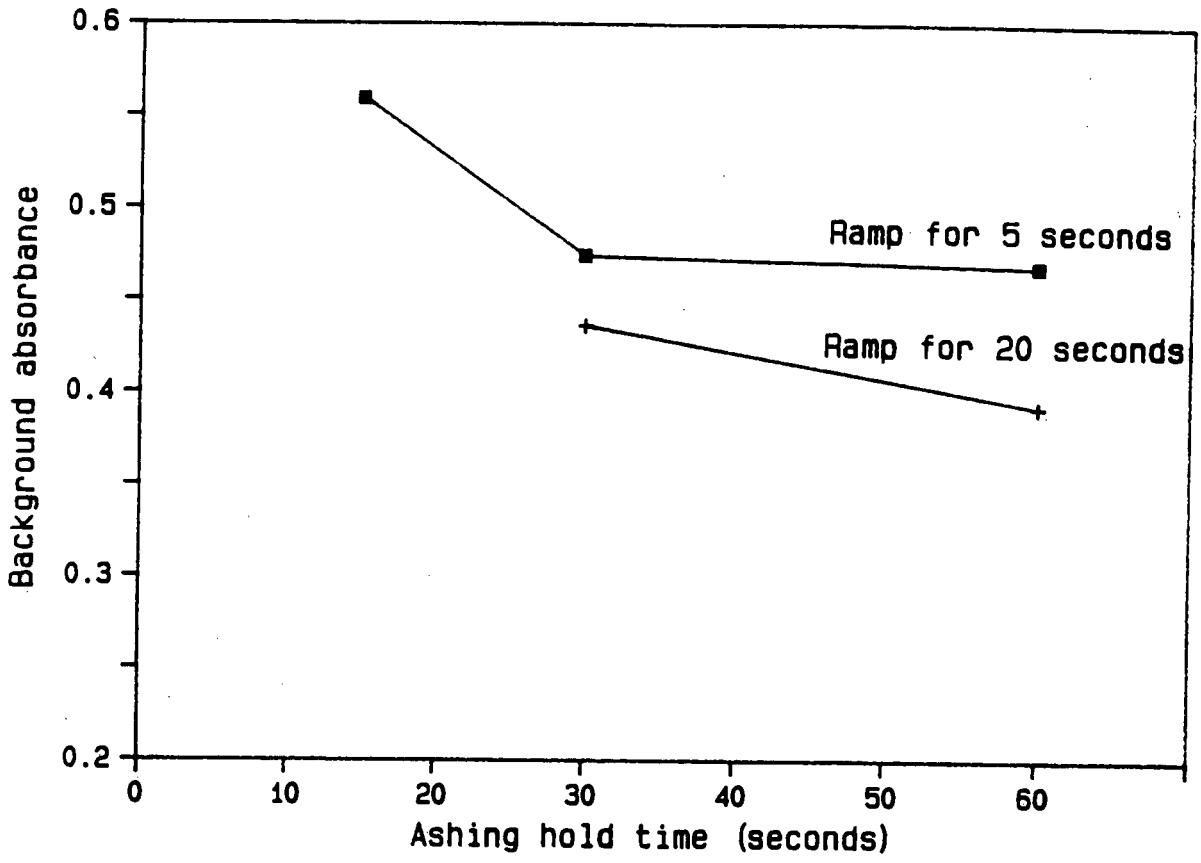


Figure 4.8: Effect of ramp and hold time on the background absorbance of NBS SRM 1632a in 20% nitric acid

4.4.2 Use of oxygen

Problems were initially experienced with poor reproducibility of coal slurries which was attributed to the use of unsuitable slurry media resulting in sample flow to the ends of the graphite tube (section 3.7.2). Ashing ramp

times were also found to affect the precision, especially with oxygen ashing. The use of short ramp times resulted in poor atomisation precision, for example, a ramp of 10 seconds gave a RSD of 22%, a 30 second ramp giving 5.5%. This was attributed to sample sputtering by rapid oxidation of the organic matter.

Preliminary studies on the use of oxygen as an ashing aid were performed using medical air. A slurry of PF 87 was prepared in 0.005% Triton X-100 and the background and background corrected signal monitored at various ashing temperatures.

A two step ashing program was utilised, the first step was in a stream of air. A second ashing step was performed in argon to remove all traces of air prior to atomisation in order to preserve the graphite tube [Gro82]. The temperatures of both steps were the same. An increase in the ashing temperature led to a decrease in the background signal (figure 4.9 (a)). An increase in sensitivity was obtained at higher ashing temperatures. At 800°C the absorbance was at least three times that at 500°C. The high temperature enhancement occurred in peak area measurements as well as in peak height measurements. This indicates that the effect is not due to an increase in atomisation rate but to the total number of absorbing atoms present. Atomisation rate increases would give taller, sharper peaks with constant integrated areas. No enhancement occurred when both ashing steps were performed in argon only (b).

The influence of air flow rate on background absorbance is illustrated in figure 4.10. Low flow rates (100ml/min) are effective in reducing the absorbance. The highest point on the curve (0.7 absorbance units) is the background absorbance in the presence of argon only.

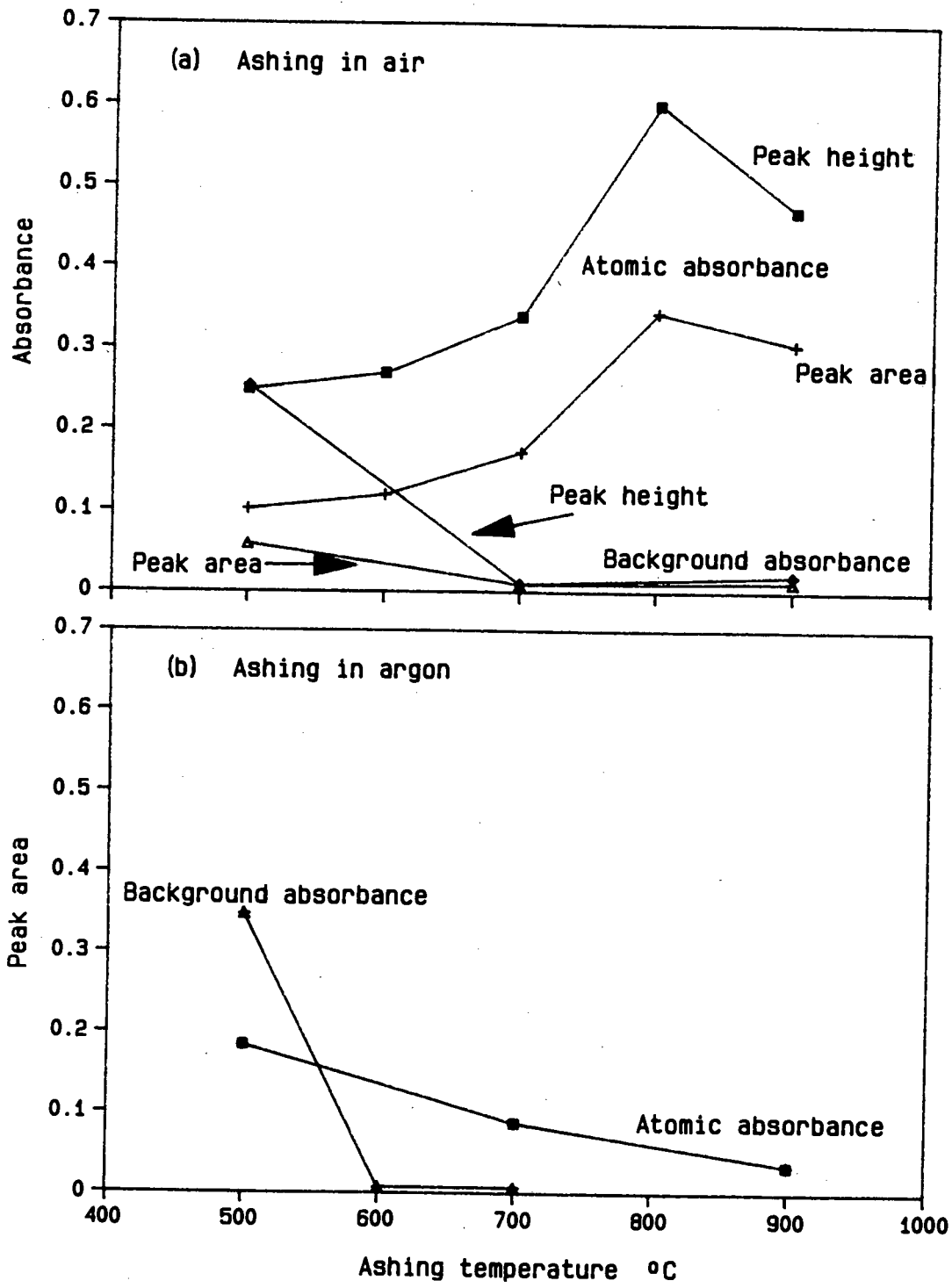


Figure 4.9: Ashing curves of PF 87 slurry

Air ash	Ash 1: Ramp 30 secs, hold 45 secs (air at 300ml/min)
	Ash 2: Ramp 1 sec, hold 15 secs (argon at 300ml/min)
Argon ash	Both ashing steps in 300ml/min argon

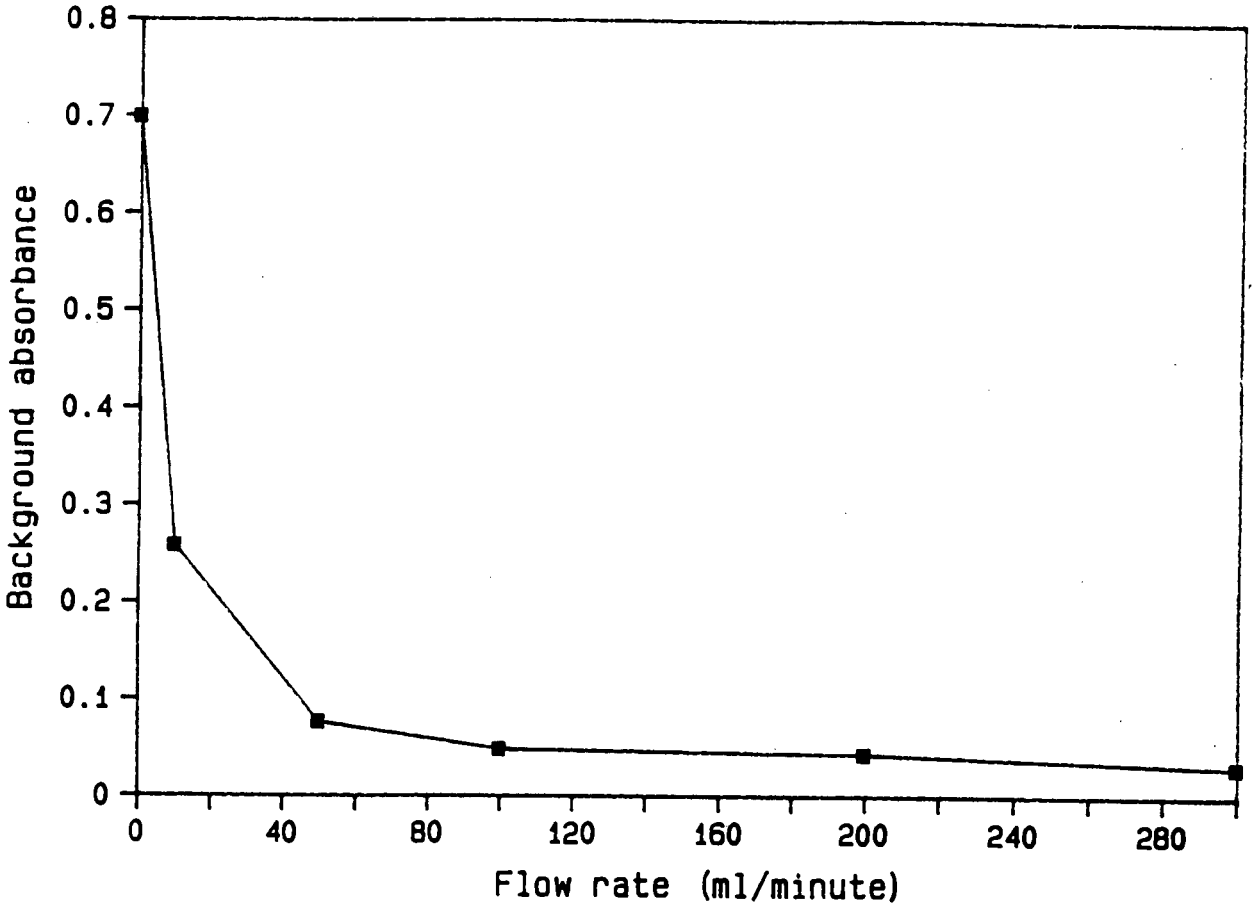
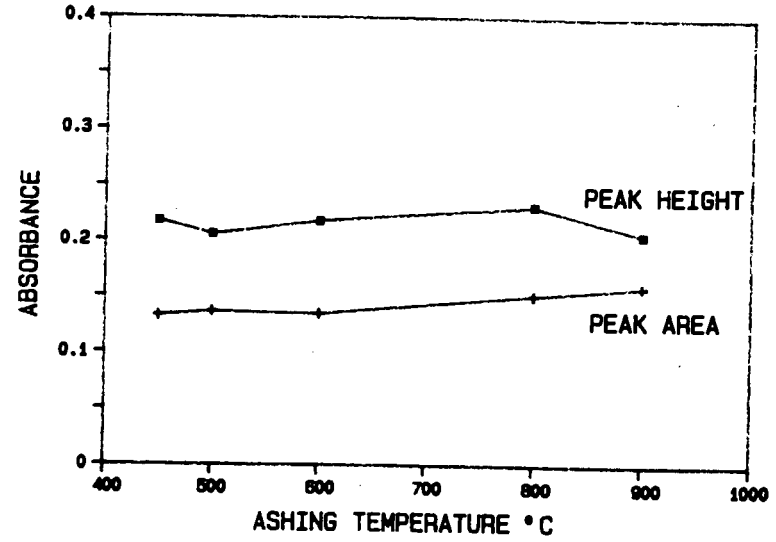


Figure 4.10: Effect of air flow rate on background absorbance of PF 91 slurry

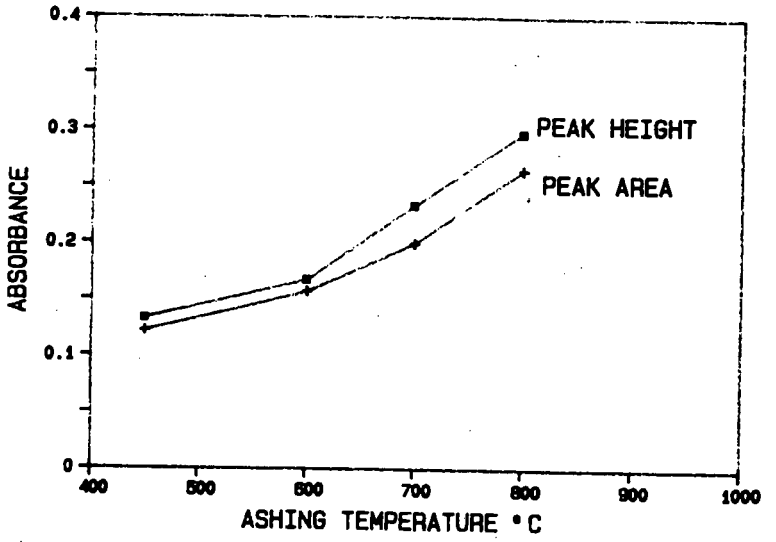
As the use of air proved promising in the removal of the problematic high background signal, further investigations were performed with oxygen.

The experiment was repeated using a different coal sample (PF 88) and an aqueous standard. No enhancement was observed in peak height or peak area for the aqueous standard (figure 4.11(a)). The ashing curve illustrates the



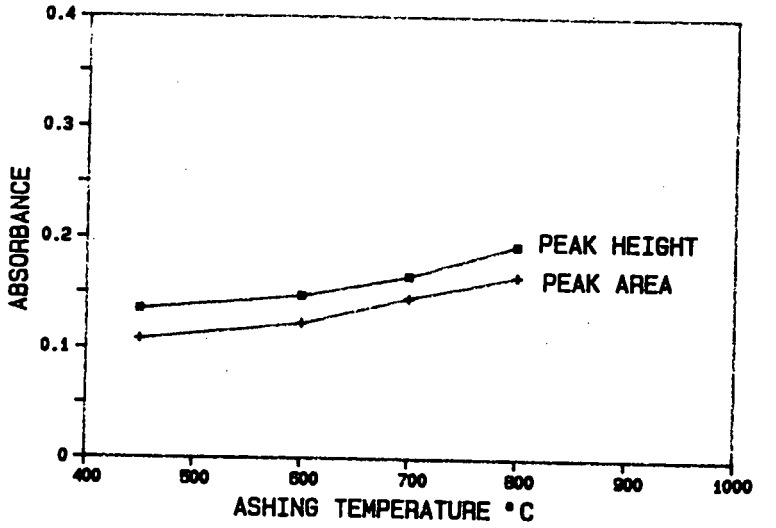
(a)

Ash 1 temperature = ash 2 temperature



(b)

Ash 1 temperature = ash 2 temperature



(c)

Ash 1 at 450° C
Ash 2 variable

Figure 4.11: Ashing curves in the presence of oxygen
(a) Aqueous standard
(b) PF 88
(c) PF 88

analyte modification effect obtained in oxygen, as in the absence of oxygen, volatilisation losses occur at ashing temperatures above 300°C (figure 4.3 (c)). A mechanism for the observed shift to higher appearance temperature has been proposed by Salmon and Holcombe [Sal82].

Peak enhancement was observed for the coal slurry (figure 4.11 (b)). At 800°C, the peaks are more than double those at 450°C. In (c), the oxygen ashing step temperature was held constant at 450°C and the argon ashing step temperature varied. The enhancement observed at 800°C is not as pronounced under these conditions. The enhancement appears to be dependent on the temperature of oxygen ashing, the effect being greater at higher temperatures. As aqueous standards did not show the same trends, the observed behaviour must be due to the coal matrix constituents. Schlemmer and Welz [Sch87] determined Cd in NBS SRM 1632a and 1632b coals using an oxygen ashing step but did not comment on any increase in sensitivity. Platform atomisation with phosphate modification was used whereas this study was performed with pyrolytically coated tubes and nitric acid.

Further work was not performed with oxygen ashing due to the observed matrix effects. Matrix modification was subsequently investigated to stabilise Cd, thus allowing elevated ashing temperatures to be employed to remove the matrix components prior to atomisation.

4.4.3 Use of matrix modifier for coal and fly ash

The effect of $NH_4H_2PO_4$ on the ashing characteristics of an aqueous standard was investigated by preparing 0.003ppm standards in various concentrations of $NH_4H_2PO_4$ solutions containing 0.2% nitric acid and 0.005% Triton X-100. Figure 4.12 illustrates the effect of modifier concentration on the

volatilisation losses. The curve reaches a plateau at approximately 1.5% modifier. A slight excess (2%) of modifier was used for further studies.

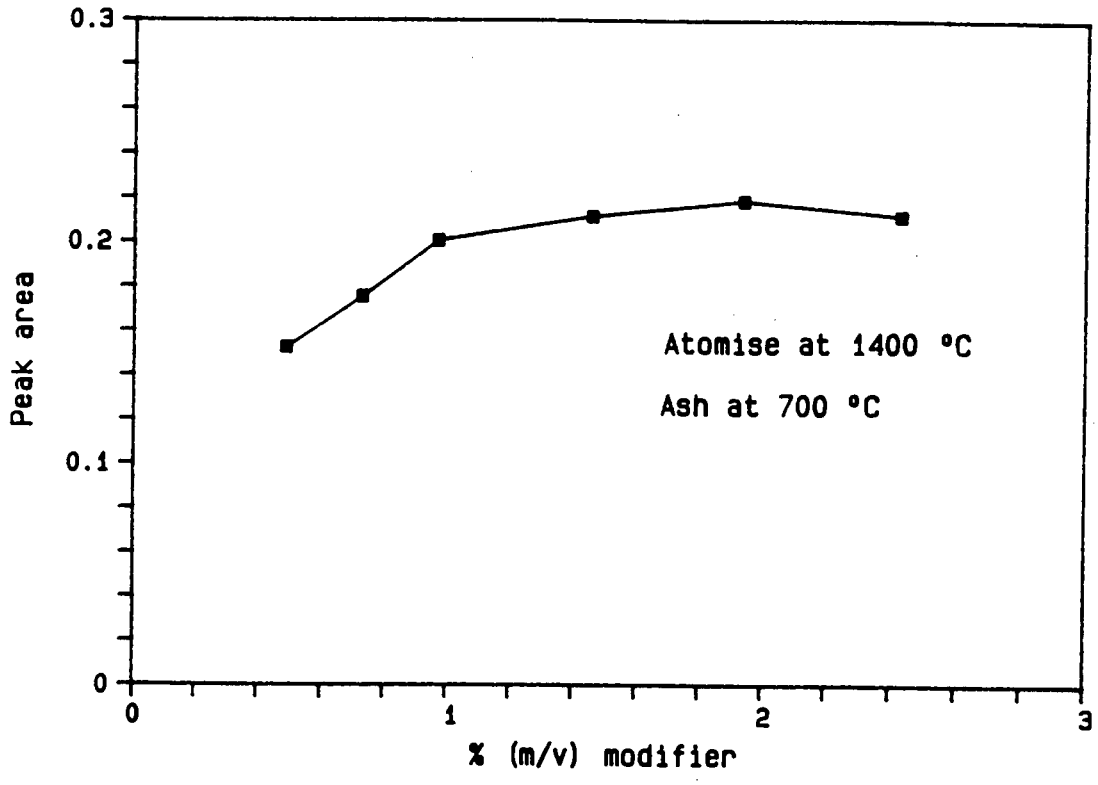


Figure 4.12: Effect of ammonium dihydrogen orthophosphate modifier concentration on the response of an aqueous cadmium solution

The ashing temperature, atomisation temperature and the internal gas flow during atomisation were found to be critical for the analysis of coal slurries in the presence of modifier solution. These effects are depicted in figure 4.13. Figure 4.13 (a) and (b) illustrates the effect of ashing temperature on the absorbance peak. An ashing

temperature of less than 700°C results in a negative peak before the absorbance peak due to volatilisation of the smoke-forming matrix components. These components are removed by ashing at higher temperatures. High atomisation temperatures (>1300°C) gives peaks with negative tails. Figure 4.13 (c) and (d) shows the atomisation peaks at 1400°C and 1300°C. At 1300°C the atomisation peak is effectively resolved from the background peak. At low internal gas flows, the residence time of the smoke in the tube is increased, leading to negative tails, the effect worsening as the gas flow is further reduced. Figure 4.13 (d), (e) and (f) illustrate the effect of gas flows of 50, 10 and 0 ml/minute. The size of the negative peak appeared to be related to the organic content of the coal as well as to the slurry concentration. Not all coal samples gave problems with background interferences, but the analytical conditions were optimised to cope with all samples. Negative peaks lead to errors in peak area evaluations as the negative area is added to the total area, thus yielding lower analytical results. Stephen et al. [Ste85] reported a similar problem with the determination of lead in spinach. As the background absorption occurred late in the atomisation peak, the deuterium arc background correction system could adequately correct for the interference at the peak maximum. Errors were obtained with peak area measurement due to the large background interference at the peak tail.

The peak profiles for fly ash are illustrated in figure 4.14. At an atomisation temperature of 1300°C the peaks are flatter and broader than at 1400°C. At 1600°C negative peaks are obtained due to the smoke-forming matrix components. Fly ash samples can therefore be effectively atomised at 1300°C or 1400°C, but the optimum atomisation temperature for coal is less flexible. If coal and fly ash samples are to be simultaneously determined an atomisation

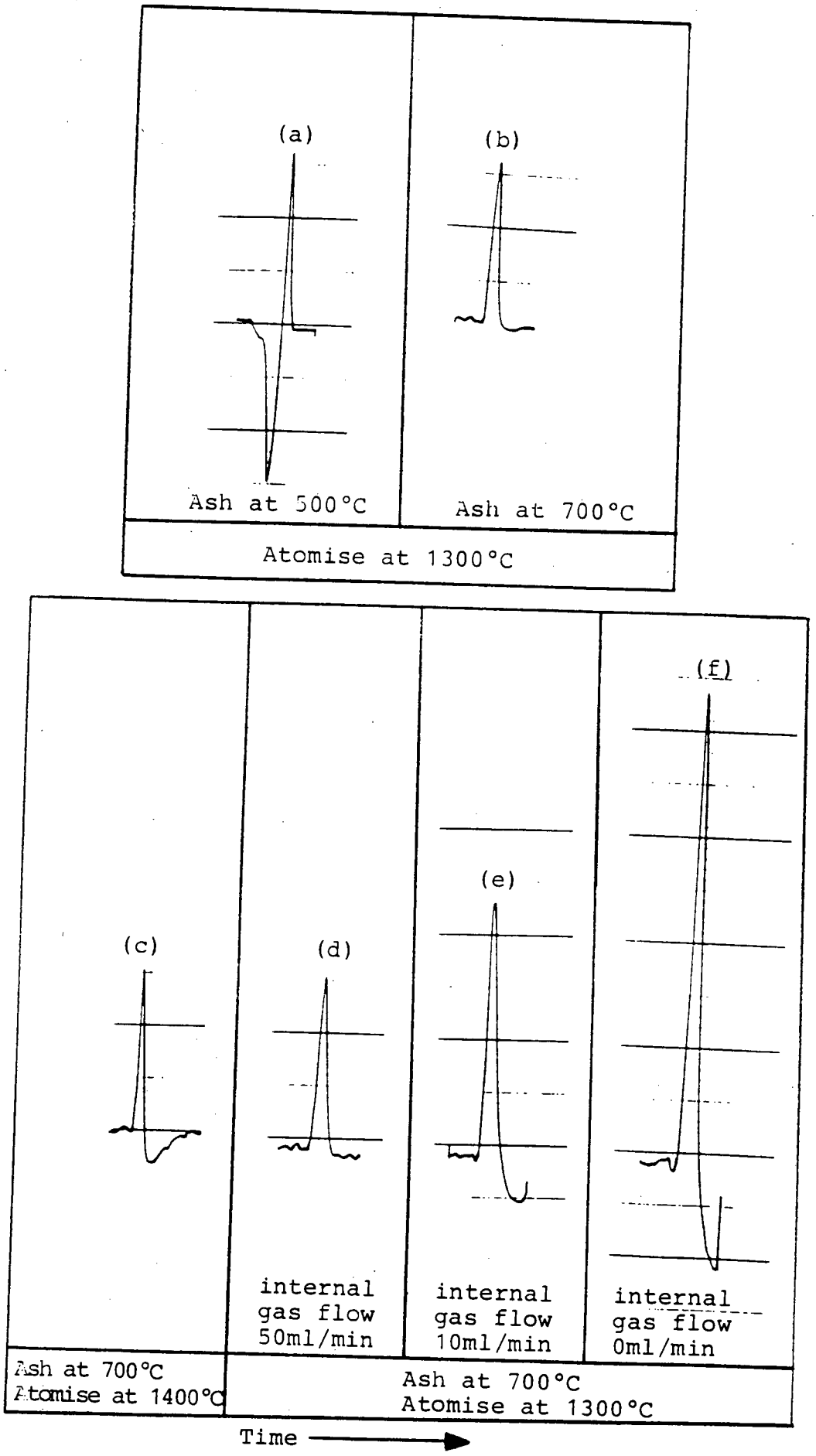


Figure 4.13: Effect of ashing temperature, atomisation temperature and gas flow rate on absorbance peaks of coal slurry.

temperature of 1300°C is required. Care must be taken that the atomisation step is sufficiently long in order to allow the absorbance peaks, especially of the fly ash, to return to the baseline. If only fly ash samples are analysed, atomisation at 1400°C is preferred, as the peaks are sharper than at 1300°C.

Ashing curves for an aqueous standard, coal slurry and fly ash slurry appear in figure 4.15. The aqueous standard and two slurries were prepared to contain 5% ethanol which is needed for dispersion of the coal slurries (see chapter 3). The addition of ethanol is not necessary for the fly ash slurries but was added in order to have a single analytical procedure for both samples. Ashing losses from the aqueous standard occurs at temperatures above 900°C compared with 300°C in the absence of modifier (figure 4.3 (c)). An ashing temperature of 700°C was chosen as optimal, no ashing losses occurred and it was found to be high enough to remove the smoke forming matrix components of the coal samples.

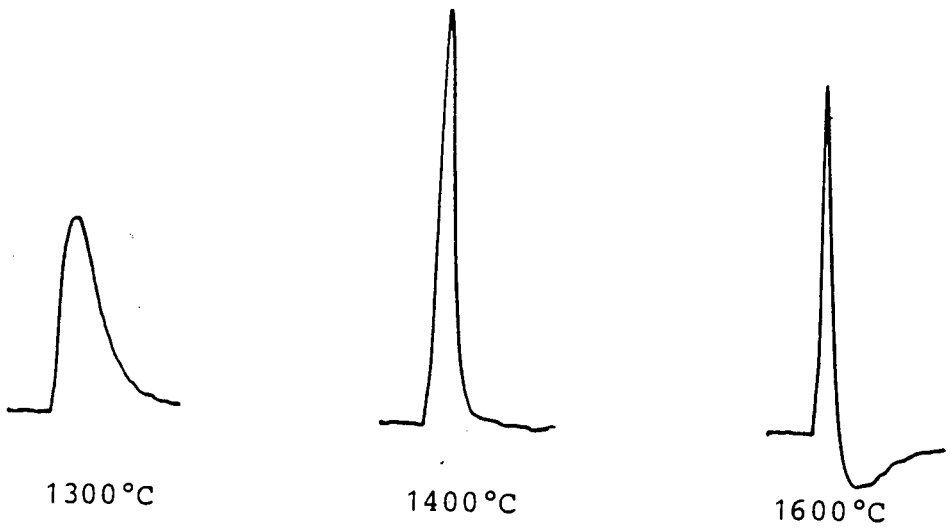


Figure 4.14: Effect of atomisation temperature on the atomisation peaks of fly ash

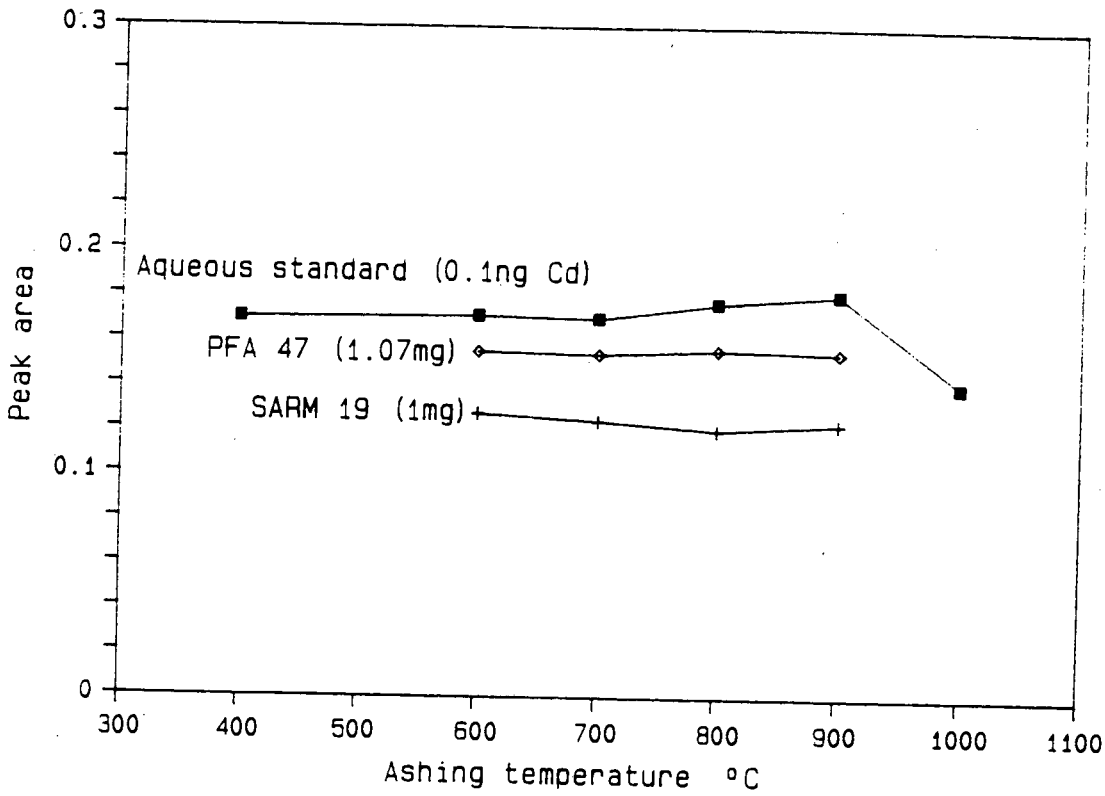


Figure 4.15: Optimisation of ashing temperature
Standard and slurries in 2% ammonium dihydrogen orthophosphate modifier solution and 5% ethanol

4.5 RESULTS AND DISCUSSION

4.5.1 Background correction system

All investigations were performed with deuterium arc background correction. It is likely that the background absorbance problems which were experienced could be eliminated or reduced with the use of more sophisticated correction systems. Several studies [Let87, Wel86] have shown that the use of background correction systems such as Zeeman-effect eliminates many of the interferences experienced with deuterium arc correction.

Welz and Schlemmer [Wel86] investigated the determination of cadmium in marine biological tissue using the STPF concept. They found Zeeman-effect background correction to be superior to deuterium backgound correction as it eliminated the spectral interference. Cadmium could be determined in some of the samples with deuterium background correction only after careful optimisation of the temperature program. With Zeeman-effect background correction, all samples could be determined routinely.

4.5.2 Determination of cadmium in fly ash using solid reference standard calibration

Cadmium was determined in the fly ash samples using calibration graphs constructed with NBS SRM 1633a fly ash slurries. The spectrophotometer and furnace operating conditions are listed in table 4.3.

Table 4.3: Operating conditions for cadmium determinations in fly ash slurries using solid reference calibration

(a) Spectrophotometer

Wavelength (nm):	228.8
Slit width (nm):	0.7
Lamp current (mA):	6
Background corrector:	On
Integration time (seconds):	6

(b) Furnace

Step	Temperature °C	Ramp (seconds)	Hold (seconds)	Internal Argon flow (ml/min)
Dry	110	5	30	300
Ash	600	5	30	300
Atomise	1400	0	5	10
Clean	2700	1	5	300

Peak area measurements were used for quantification. Several samples were determined using peak height measurements. The results appear in table 4.4.

In most cases, peak height and peak area results compare favourably, indicating that the atomisation responses of the fly ash samples are similar to those of the solid standard. However, this is not always the case and peak area measurements are preferred as they minimise the problem of matrix dependent peak shapes [Ebd87] as well as particle size effects. This is demonstrated by the following experiment. A fly ash sample (PFA 1) was ground for various time intervals in the swing mill and the cadmium concentration in the various portions determined using peak height and peak area measurements. The results appear in table 4.5. As the particle size decreases (longer grinding time) the results obtained with peak height measurements increase as the atomisation peaks become higher and

Table 4.4: Determination of cadmium in fly ash: calibration with NBS SRM 1633a.

Sample	Origin	µg Cd/g	
		Peak heights	Peak areas
PFA 1	ARNOT BLR4 PFA RH1 PR		0.13 ± 0.005 (c)
PFA 2	ARNOT BLR4 PFA RH2 PR		0.28
PFA 6	CAMDEN BLR 4 PFA LH1 PR		0.30
PFA 13	CAMDEN BLR 6 PFA LH2 PR		0.22
PFA 15	CAMDEN BLR 6 PFA RH ECON PR		0.06
PFA 18	DUVHA BLR 1 PFA LH ROW 2 PR	0.63	0.66 ± 0.09 (a)
PFA 19	DUVHA BLR 1 PFA LH ROW 3 PR	1.05	1.03
PFA 20	DUVHA BLR 1 PFA LH ROW 4 PR	1.45 ± 0.02 (a)	1.21 ± 0.10 (a)
PFA 21	DUVHA BLR 1 PFA RH ROW 1 PR	0.20	0.26
PFA 22	DUVHA BLR 1 PFA RH ROW 2 PR	0.61 ± 0.15 (a)	0.58 ± 0.03 (a)
PFA 23	DUVHA BLR 1 PFA RH ROW 3 PR	1.16 ± 0.02 (a)	0.98 ± 0.02 (a)
PFA 34	KOMATI BLR 7 PFA PR		0.12 ± 0.01 (b)
PFA 42	KRIEL BLR 6 PFA 2 PR		0.04
PFA 45	MATLA BLR 1 PFA LH1 PR		0.08 ± 0.003 (d)
PFA 46	MATLA BLR 1 PFA LH2 PR	0.05	0.05 ± 0.004 (a)
PFA 47	MATLA BLR 1 PFA LH3 PR		0.10
PFA 48	MATLA BLR 1 PFA LH4 PR	0.18	0.16 ± 0.002 (a)
PFA 49	MATLA BLR 1 PFA LH5 PR		0.08
PFA 50	MATLA BLR 1 PFA LH6 PR		0.08
PFA 51	MATLA BLR 1 PFA LH7 PR	0.10	0.11 ± 0.01 (d)
PFA 53	MATLA BLR 1 PFA RH1 PR	0.08 ± 0.002 (a)	0.08 ± 0.01 (a)
PFA 54	MATLA BLR 1 PFA RH2 PR	0.04	0.05 ± 0.01 (a)
PFA 55	MATLA BLR 1 PFA RH3 PR	0.07	0.07
PFA 56	MATLA BLR 1 PFA RH4 PR	0.15	0.15
PFA 57	MATLA BLR 1 PFA RH5 PR	0.04 ± 0.002 (a)	0.04
PFA 58	MATLA BLR 1 PFA RH6 PR	0.05	0.06 ± 0.01 (f)
PFA 59	MATLA BLR 1 PFA RH7 PR	0.09	0.09
PFA 60	MATLA BLR 1 PFA RH8 PR	0.13	0.12
PFA 67	MATLA TEST 2 PFA RH2 PR		0.08
PFA 68	MATLA TEST 2 PFA RH3 PR		0.15
PFA 69	MATLA TEST 2 PFA RH4 PR		0.20 ± 0.01 (b)

Key: All results single determinations except
(a) Average of 2
(b) Average of 3
(c) Average of 4
(d) Average of 7
(e) Average of 10
(f) Average of 11

narrower. Peak area determinations remain relatively constant. The effect of particle size on atomisation peaks is also illustrated by figure 3.7. This figure depicts the peaks obtained with PFA 9 ground for various times in the ball mill. Increasing the grinding time not only improves the precision, but results in higher, narrower peaks. It appears that good agreement between peak height and peak area determination is coincidental, consequently all further determinations were made with peak area measurements.

Table 4.5: Effect of grinding time on the determination of PFA 1 using peak area and peak height measurements

Grinding time (minutes)	Cadmium concentration µg/g	
	Peak area	Peak heights
5	0.132	0.168
10	0.138	0.188
15	0.136	0.215
20	0.127	0.211

Table 4.6 compares the results obtained with the standard addition and calibration graph techniques. The agreement between the results indicate that the slopes of the standard addition graphs and the calibration graphs are similar. Analysis with a calibration graph is preferred as it is less time-consuming than the standard addition technique.

Table 4.6: Determination of cadmium in fly ash - comparison of standard addition and calibration graph methods using solid reference standard

Sample	Origin	Cadmium concentration µg/g	
		Standard addition	Calibration graph
PFA 57	MATLA BLR 1 PFA RH5 PR	0.05	0.04
PFA 58	MATLA BLR 1 PFA RH6 PR	0.06	0.06 ± 0.01 (f)
PFA 59	MATLA BLR 1 PFA RH7 PR	0.09	0.09
PFA 60	MATLA BLR 1 PFA RH8 PR	0.12	0.12

All results single determinations except (f) average of 11 determinations

4.5.3 Determination of cadmium in coal and fly ash using aqueous standard calibration

4.5.3.1 Linearity and detection limit

Figure 4.16 illustrates a typical aqueous calibration graph for cadmium determinations. Excellent linearity to at least 100pg Cd was obtained (r=0.99918).

The detection limit was 2.9pg Cd and was calculated using the following formula:

$$\frac{3 \times (s.d.)_{blank}}{S}$$

where: $(s.d.)_{blank}$ = standard deviation of blank solution (10 readings)

S = slope of calibration graph

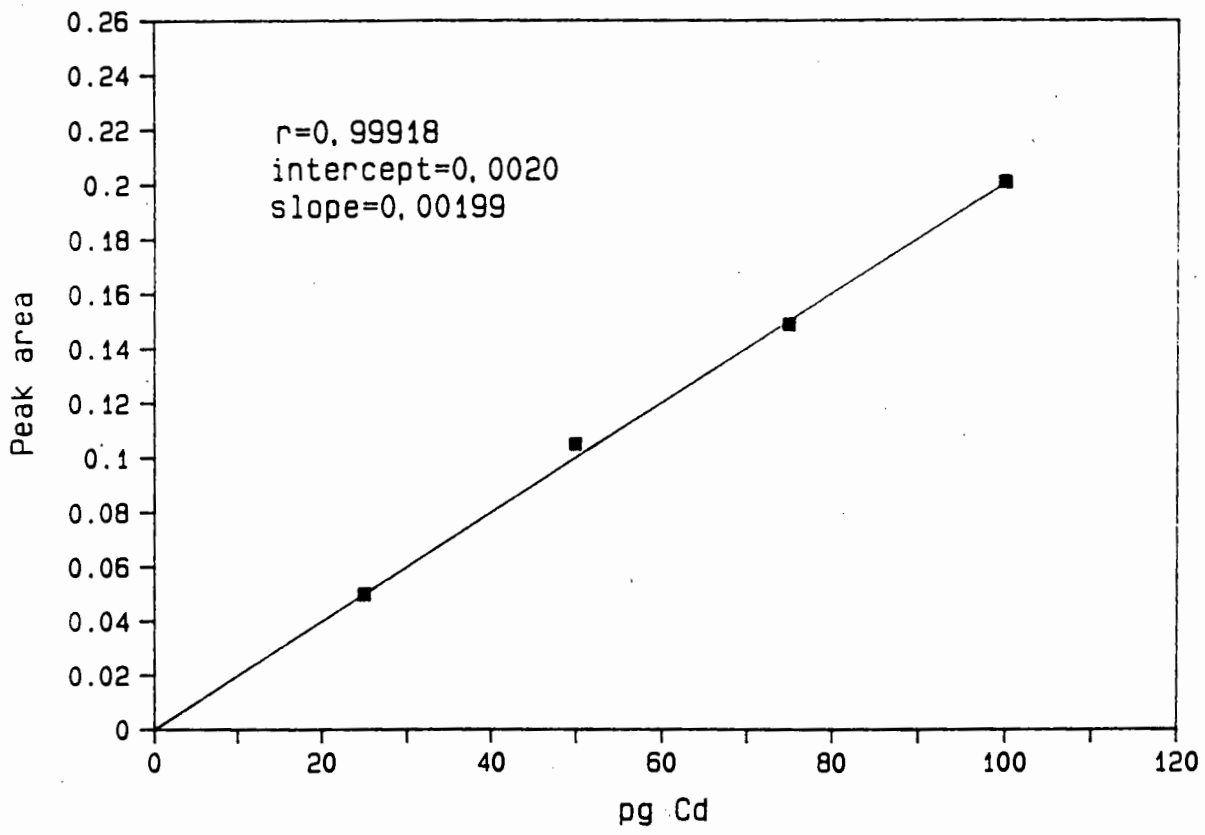


Figure 4.16: Calibration graph for cadmium determinations

4.5.3.2 Analysis of coal and fly ash samples

The method initially developed for the determination of cadmium in coal slurries, was found to be applicable to fly ash analysis. Table 4.7 compares the aqueous standard calibration method, with matrix modifier, to the solid reference standard calibration method. Excellent agreement was obtained between the two methods. The aqueous standard calibration method is preferred as expensive solid reference standards are not required for calibration purposes, as is the need for separate coal and fly ash solid standards.

The accuracy of the aqueous calibration method was evaluated by analysing reference coal and fly ash samples (table 4.8). Acceptable results were obtained for the NBS SRM standards. The NBS SRM 1635 result is slightly low, but was felt to be acceptable at such low cadmium concentrations (0.03μg/g). The precision (as %RSD) was better than 31%, which compares well with the 33% RSD certified for NBS SRM 1635. The injection precision is included in the table.

The cadmium concentrations in the SARM standards are not certified, due to the data having very high robust standard deviations [Rin84]. The statistical data for the cadmium analysis in these reference materials are given in table 4.9.

Table 4.7: Comparison of aqueous and solid reference standard calibration results

Sample	µg Cd per g Calibration procedure	
	Solid reference NBS SRM 1633a	Aqueous standards
PFA 23	0.98 ± 0.02	1.12 ± 0.13
PFA 46	0.05 ± 0.004	0.05 ± 0.002
PFA 48	0.16 ± 0.002	0.16 ± 0.002
PFA 51	0.11 ± 0.01 (c)	0.10 ± 0.01 (a)
PFA 58	0.06 ± 0.01 (d)	0.07 ± 0.01
NBS SRM 1633a		1.10 ± 0.07 (b)

All results are the average of 2 determinations, except
(a) average of 3 determinations
(b) average of 4 determinations
(c) average of 7 determinations
(d) average of 11 determinations

Table 4.8: Analysis of slurried reference coals and fly ash using matrix modification and aqueous standard calibration

Sample	Slurry analysis				Certified value µg Cd/g	Other work * µg Cd/g
	Number of determinations	%RSD	µg Cd/g	Injection %RSD @		
NBS SRM 1633a	4	6.7	1.10 ± 0.07	2.8	1.0 ± 0.15	1.02 ± 0.11
NBS SRM 1632a	7	17.2	0.13 ± 0.02	11.4	0.17 ± 0.02	0.150 ± 0.017
NBS SRM 1635	3	6.3	0.02 ± 0.001	13.6	0.03 ± 0.01	
SARM 18	3	30.8	0.01 ± 0.004	16.3		
SARM 19	4	13.2	0.08 ± 0.01	11.6		
SARM 20	4	18.0	0.06 ± 0.01	13.0		

@ Average of 5 injections
* From Sch87, average of 10 determinations, solid sampling technique

Table 4.9: Cadmium in SARM coals [Rin84]

Sample	N	RSD (%)	Robust RSD (%)	Mean	Median	Gastwirth Median	DCM
SARM 18	7	85	127	0.10	0.07	0.06	0.05
SARM 19	9	95	290	0.42	0.16	0.26	0.13
SARM 20	9	125	649	0.55	0.11	0.24	0.095

Where:
N: number of bottle means
RSD (%): relative standard deviation
DCM: dominant cluster mode

The results of the analysis of South African coal samples using the matrix modifier method appear in table 4.10. Results obtained for the fly ash using calibration with NBS SRM 1633a are included for comparison. The median concentration for cadmium in the coal samples was 0.05µg/g and 0.12µg/g in the fly ash samples.

The results are depicted graphically in figures 4.17 (Matla), 4.18 (Duvha) and 4.19 (Arnot, Camden and Komati). In all cases, cadmium levels in the fly ash are greater than those in the corresponding coal. A general trend of increasing cadmium concentration with consecutive precipitators was noted, especially with the Duvha and Arnot samples (figures 4.18 and 4.19). Willis [Wil82] determined the elemental concentrations of the coal and fly ash samples analysed in this study using X-Ray Fluorescence Spectrometry. He observed that many volatile minor and trace elements were progressively enriched in fly ashes from sequential precipitators.

Willis also found an enrichment factor of 4.5 for elements in the Duvha fly ash relative to the coal. Cadmium was not determined in his study as XRF spectrometry lacks the sensitivity to determine such low levels. Using an ash content of 23.4% [Wil82], cadmium in the LH ROW 4 precipitator is enriched 3.1 times relative to the coal.

Table 4.10: Cadmium in slurried coal and fly ash

Sample	Origin	Cadmium concentration µg/g	
		Coal	Fly ash
PF 87	ARNOT BLR 4 COAL	0.07 ± 0.01 (b)	
PFA 1	ARNOT BLR4 PFA RH1 PR		0.13 ± 0.005 (c)
PFA 2	ARNOT BLR4 PFA RH2 PR		0.28
PF 89	CAMDEN BLR 6 COAL	0.02 ± 0.001 (a)	
PFA 6	CAMDEN BLR 4 PFA LH1 PR		0.30
PFA 13	CAMDEN BLR 6 PFA LH2 PR		0.22
PFA 15	CAMDEN BLR 6 PFA RH ECON PR		0.06
PF 90	DUVHA BLR 1 COAL	0.09 ± 0.01 (b)	
PFA 18	DUVHA BLR 1 PFA LH ROW 2 PR		0.66 ± 0.09 (a)
PFA 19	DUVHA BLR 1 PFA LH ROW 3 PR		1.03
PFA 20	DUVHA BLR 1 PFA LH ROW 4 PR		1.21 ± 0.10 (a)
PFA 21	DUVHA BLR 1 PFA RH ROW 1 PR		0.26
PFA 22	DUVHA BLR 1 PFA RH ROW 2 PR		0.58 ± 0.03 (a)
PFA 23	DUVHA BLR 1 PFA RH ROW 3 PR		0.98 ± 0.02 (a)
PF 93	KOMATI BLR 1 COAL	0.06 ± 0.02 (b)	
PF 94	KOMATI BLR 2 COAL	0.08	
PF 95	KOMATI BLR 6 COAL	0.05	
PF 96	KOMATI BLR 7 COAL	0.06	
PF 97	KOMATI BLR 8 COAL	0.06	
PF 98	KOMATI BLR 9 COAL	0.03	
PFA 34	KOMATI BLR 7 PFA PR		0.12 ± 0.01 (b)
PF 99	KRIEL BLR 1 COAL	0.01 ± 0.001 (a)	
PFA 42	KRIEL BLR 6 PFA 2 PR		0.04
PF 101	MATLA BLR 1 COAL	0.01 ± 0.001 (a)	
PFA 45	MATLA BLR 1 PFA LH1 PR		0.08 ± 0.003 (d)
PFA 46	MATLA BLR 1 PFA LH2 PR		0.05 ± 0.004 (a)
PFA 47	MATLA BLR 1 PFA LH3 PR		0.10
PFA 48	MATLA BLR 1 PFA LH4 PR		0.16 ± 0.002 (a)
PFA 49	MATLA BLR 1 PFA LH5 PR		0.080
PFA 50	MATLA BLR 1 PFA LH6 PR		0.08
PFA 51	MATLA BLR 1 PFA LH7 PR		0.11 ± 0.01 (d)
PFA 53	MATLA BLR 1 PFA RH1 PR		0.08 ± 0.01 (a)
PFA 54	MATLA BLR 1 PFA RH2 PR		0.05 ± 0.01 (a)
PFA 55	MATLA BLR 1 PFA RH3 PR		0.07
PFA 56	MATLA BLR 1 PFA RH4 PR		0.15
PFA 57	MATLA BLR 1 PFA RH5 PR		0.04
PFA 58	MATLA BLR 1 PFA RH6 PR		0.06 ± 0.01 (f)
PFA 59	MATLA BLR 1 PFA RH7 PR		0.09
PFA 60	MATLA BLR 1 PFA RH8 PR		0.12
PFA 67	MATLA TEST 2 PFA RH2 PR		0.08
PFA 68	MATLA TEST 2 PFA RH3 PR		0.15
PFA 69	MATLA TEST 2 PFA RH4 PR		0.20 ± 0.01 (b)
PF 91	HENDRINA BLR 5 COAL	0.02 ± 0.01 (b)	
PF 102	WILGE BLR 6 COAL	0.01 ± 0.001 (a)	

Key: All results single determinations except
- (a) Average of 2
- (b) Average of 3
- (c) Average of 4
- (d) Average of 7
- (e) Average of 10
- (f) Average of 11

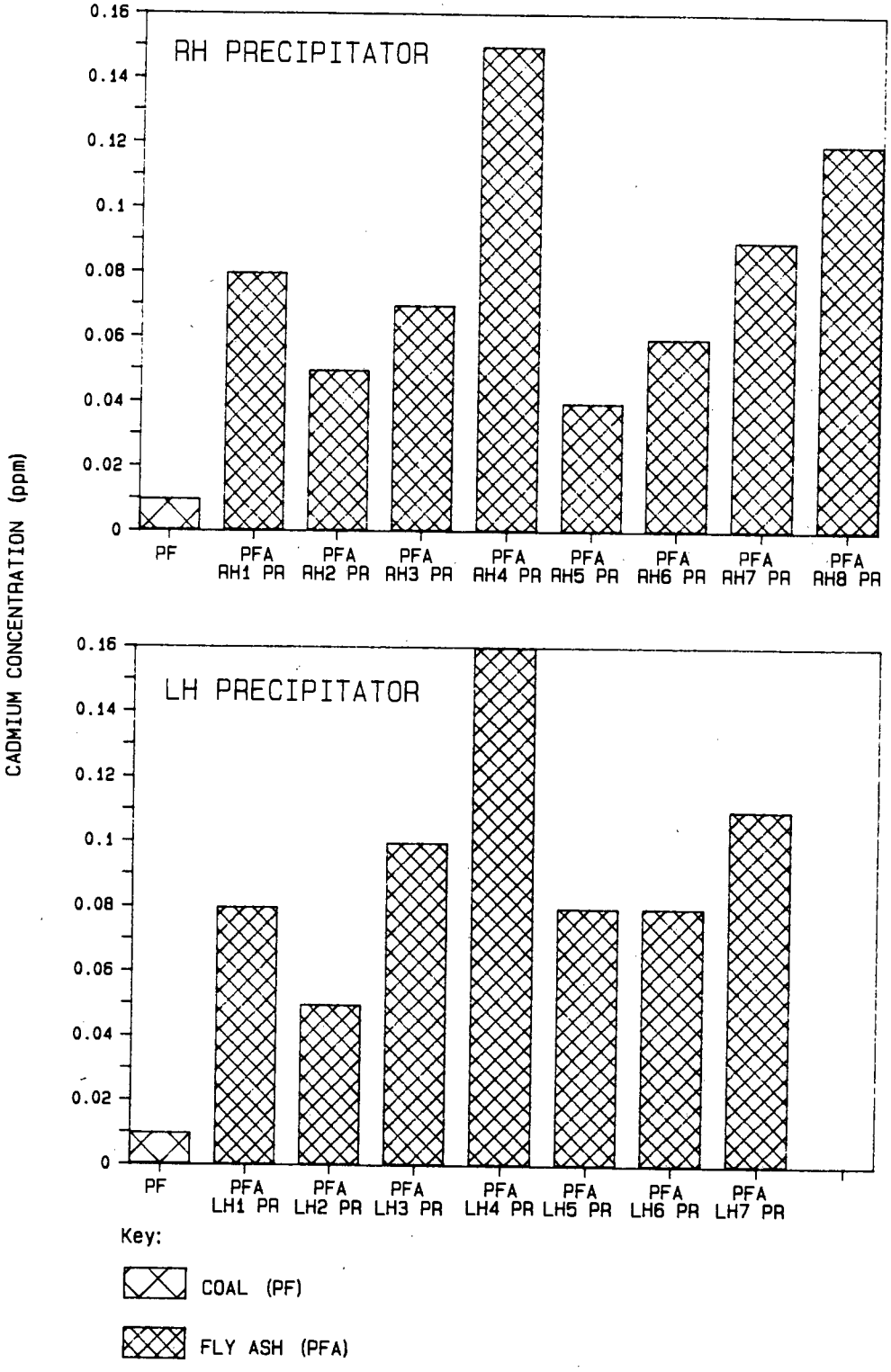


Figure 4.17: Cadmium concentration in Matla Blr 1 coal and fly ashes

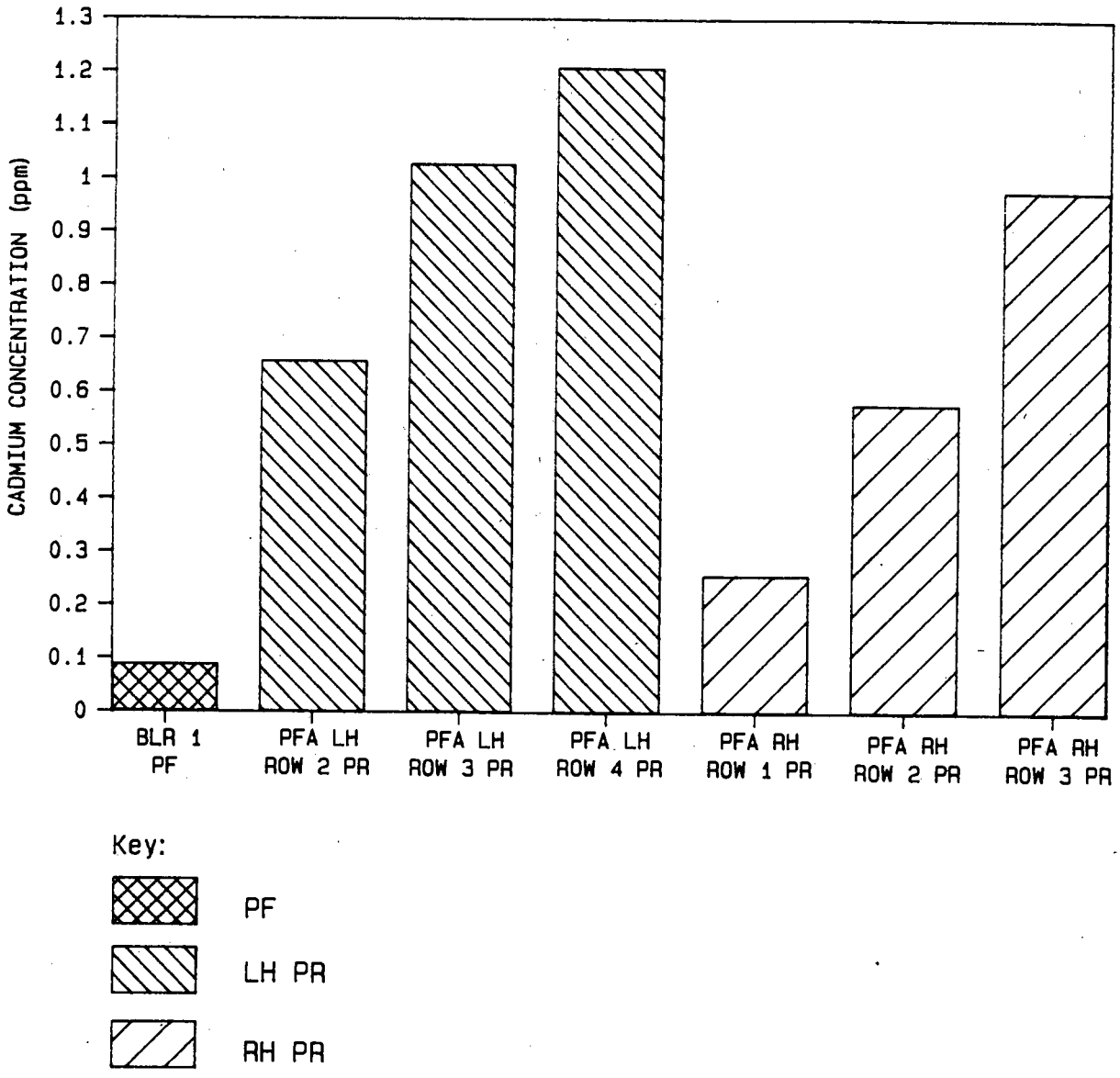


Figure 4.18: Cadmium concentration in Duvha coal and fly ashes

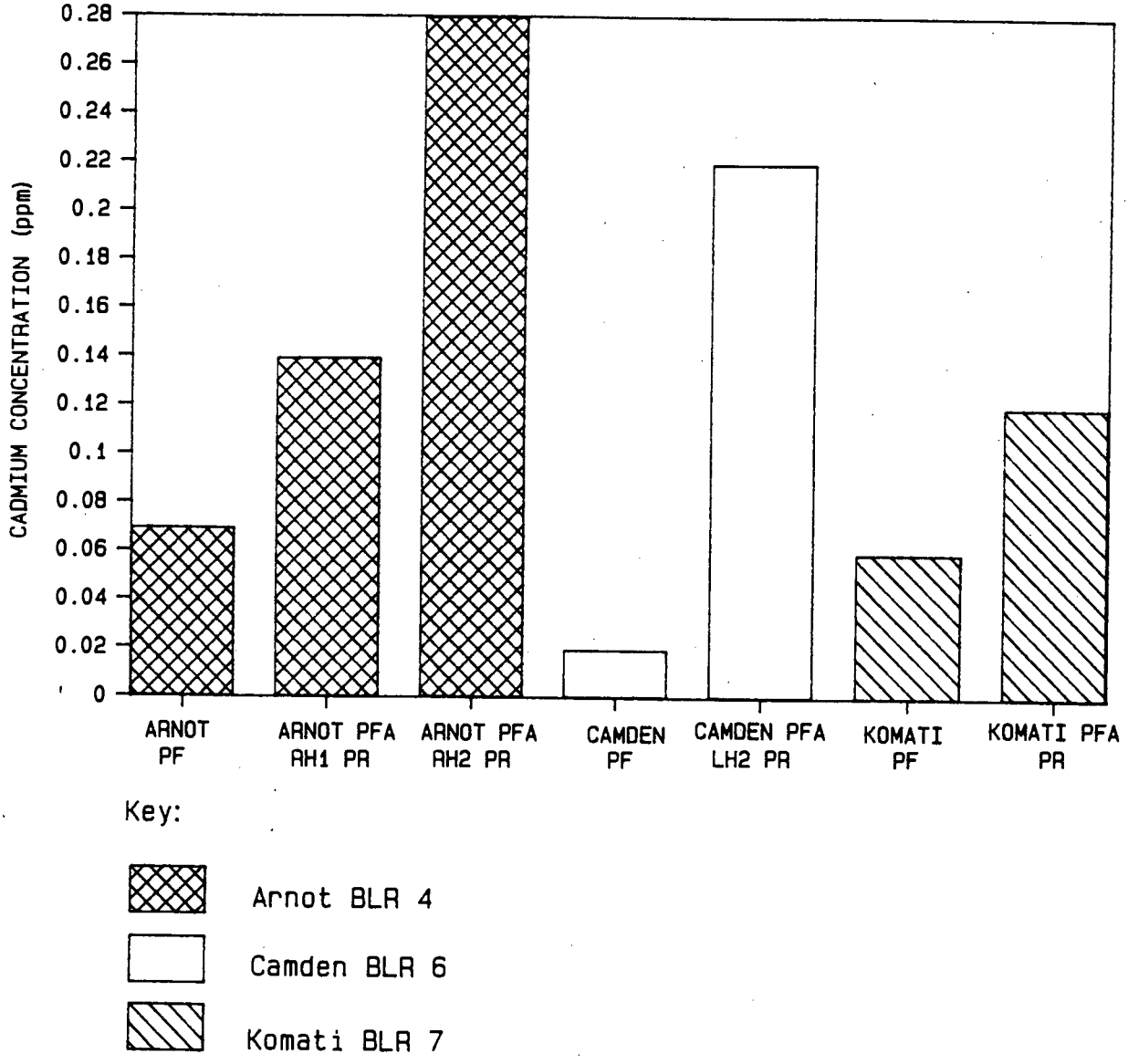


Figure 4.19: Cadmium concentration in Arnot, Camden and Komati coals and fly ashes

Similarly, the Matla boiler 1 coal has an ash content of 24.4% (see table 4.2) and the fly ash in the LH4 precipitator is enriched 3.9 times. The Arnot RH2 precipitator fly ash shows no enrichment relative to the coal. Willis [Wil82] noted that the degree of enrichment varied between power stations and attributed this to the use of different burners and fly ash collection systems.

Approximately 30 dried, ground samples (single determinations) could be determined in a 8.5 hour day with a single tube (about 200 firings).

The precision of the method (quoted as %RSD) for three coals and three fly ash samples ~~are~~ is given in table 4.11. The injection precision for several samples is included in the table.

Table 4.11: Precision of determination and injection for cadmium in South African coal and fly ash

Sample	Origin	Determination			Injection % RSD (n=5)
		n	% RSD	µg Cd/g	
PF 87	ARNOT BLR 4 COAL	3	10.3	0.07	7.3
PF 90	DUVHA BLR 1 COAL	3	11.1	0.09	5.4
PF 93	KOMATI BLR 1 COAL	3	26.3	0.06	23.6
PFA 34	KOMATI BLR 7 PFA PR	3	4.9	0.12	1.5
PFA 51	MATLA BLR 1 PFA LH7 PR	7	9.1	0.11	6.1
PFA 58	MATLA BLR 1 PFA RH6 PR	11	16.7	0.06	9.3
PFA 69	MATLA TEST 2 PFA RH4 PR	3	6.4	0.20	2.2

Calibration is with aqueous standards and the results are calculated with peak area measurements. A single method is used for both coal and fly ash samples even though the volatility of the matrices were shown to be vastly different.

The accuracy of the method was evaluated by analysing standard reference materials and the precision by performing several analyses of the same sample. Both were found to be acceptable.

5

DETERMINATION OF BERYLLIUM IN COAL AND FLY ASH

5.1 INTRODUCTION

Methods for the determination of trace quantities of beryllium usually involve the solvent extraction of the beryllium acetylacetonate complex . The resulting extract is then analysed by spectrophotometry or fluorimetry [Sto86], or graphite furnace atomic absorption spectrophotometry [Sch88, Cam78]. The extraction of beryllium acetylacetonate with isolation of beryllium from co-extracted interfering elements by cation-exchange, followed by flame AAS has been reported [Kor76, Kor76/2]. These sample preparation procedures are often complex involving extensive sample manipulation.

The acid digested samples have also been analysed directly by ICP-AES [Pou85, Kur87] and GFAAS [Gel79, Bet86, Van88].

In GFAAS, the formation of diberyllium carbide is minimised by the use of pyrocoated tubes or tubes treated with a carbide forming element [Run75]. Various modifiers, including aluminium nitrate [Mae78], ammonium hydroxide [Wel86], calcium oxide [Tho75] and magnesium nitrate [Sla83, Man83, Bet86, Van88] have been used to stabilise beryllium to allow higher ashing temperatures. Shan et al. [Sha89] determined beryllium in urine using pyrolytically coated tubes. They studied the effects of various matrix modifiers on the maximum tolerable charring temperature and the enhancement factor obtained relative to no modifier. They found that the sensitivity using a modifier of ammonium 12-molybdophosphate and ascorbic acid was improved by a factor of 1.5 in comparison with that obtained using magnesium nitrate.

STPF technology has been applied to the determination of beryllium in various matrices. Vanhoe et al. [Van88] investigated the determination of beryllium in acid digested

environmental samples using GFAAS with platform atomisation. They studied three experimental procedures: no modifier, with magnesium nitrate modifier and treatment of platforms with thorium nitrate. They concluded that when the beryllium concentration is greater than 1μg/g, addition of magnesium nitrate yields accurate and precise results. For low concentrations (below 1μg/g), they recommend treatment of the platform with thorium nitrate as no beryllium blank is introduced, as occurs with magnesium nitrate. Standard additions are necessary with the thorium nitrate procedure.

Bettinelli et al. [Bet86] reported on the determination of beryllium in acid digested NBS fly ash reference materials, using platform atomisation with magnesium nitrate matrix modification. Results were obtained using integrated peak area measurements and both the calibration graph and standard addition techniques. Good agreement with the values reported by NBS were obtained. Manning and Slavin [Man83] used platform atomisation and magnesium matrix modification for the determination of beryllium in natural water samples.

Ellis et al. [Ell88] investigated the effects of Al, Ca, Ce Cr, La, Mg, Mn, Mo, Si, Sr, H_2SO_4, W, Fe and Cu on the determination of beryllium with platform atomisation. Using peak height mode, pronounced interferences were observed from many of the elements due to changes in peak shape relative to the Be standard in nitric acid. In peak area mode however, only Mo and W interfered. High concentrations of Mo (of the order of 1000mg/l) enhanced the absorbance of Be (5 μg/l). The effect of W was small and resulted in a decrease of Be absorbance.

Styris and Redfield [Sty87] used mass spectrometry to study the gas-phase species produced in a graphite furnace containing beryllium and magnesium modifier in order to

elucidate the mechanisms involved. They concluded that stabilisation of beryllium occurs by dehydration of the dihydroxide by magnesium oxide and that during atomisation, free beryllium was produced by the thermal decomposition of the adsorbed monomeric oxide. Shan et al. [Sha89] attributed the enhancement effect observed when using ammonium 12-molybdophosphate on the beryllium signal to the formation of a larger amount of BeO, the precursor of free beryllium.

Relatively few investigations have been concerned with the direct determination of beryllium in solid samples using GFAAS (tables 2.2 and 2.3). Gladney [Gla77] determined beryllium in NBS SRM 1632 coal using a solid sampling spoon for introduction of the powdered sample. Aqueous standards were used for calibration with both the calibration graph and standard addition techniques. In both cases, excellent agreement with the certified value was obtained, and the precision was better than ±10%.

5.2 METHOD DEVELOPMENT

5.2.1 Studies with uncoated graphite tubes

Perkin-Elmer recommend the following conditions for beryllium determinations:

Table 5.1: Perkin-Elmer conditions for Be

Diluent:	0.2% nitric acid
Ash:	1000°C
Atomise:	2600°C
Tube:	Uncoated

Preliminary investigations were thus undertaken using uncoated graphite tubes.

Dilute nitric acid is recommended for the preparation of sample and standard solutions. The effect of nitric acid concentration on the response of a coal (SARM 20) slurry and a standard aqueous solution was studied and is illustrated in figure 5.1. The response of the aqueous standard increases with increasing nitric acid concentration, reaching a plateau at concentrations greater than about 5% (approximately 0.52M). Nitric acid appears to depress the peak height response for the coal slurry, with the peak area response remaining relatively constant. The decrease in peak height may indicate a slower rate of atom formation as opposed to analyte loss, as the total number of Be atoms remains constant, as reflected in the peak area measurement.

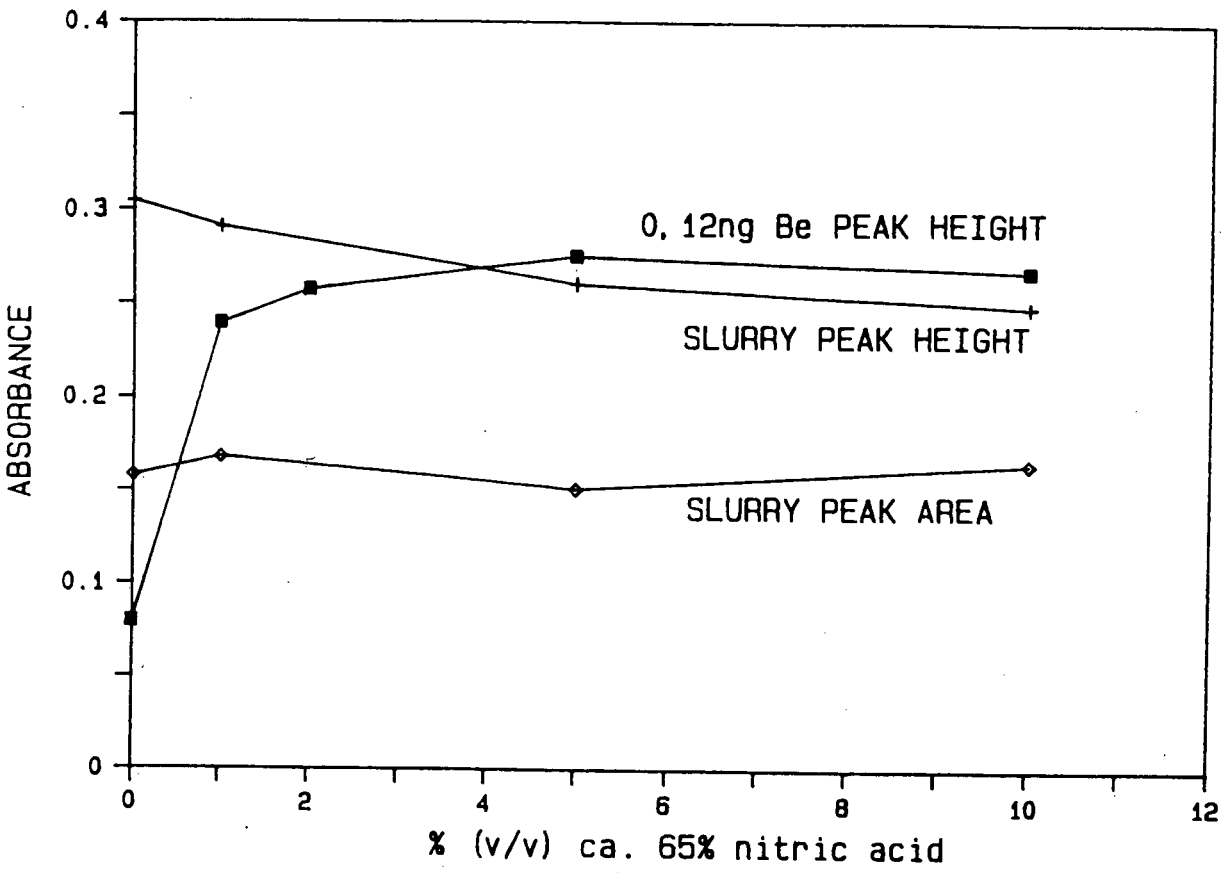


Figure 5.1: Effect of nitric acid on the response of a coal slurry (SARM 20) and an aqueous Be standard

The optimum ashing and atomisation conditions for an aqueous beryllium standard and a coal slurry (both in 0.005% Triton X-100 and 5% nitric acid) were determined. The furnace and spectrophotometer conditions are listed in table 5.2. Beryllium was determined in the SARM coals to validate the procedure. The results are in Table 5.3. In all cases, the results obtained are higher than the certified values. The positive bias in the results may have been due to matrix interferences, thus the use of a matrix modifier was investigated.

Table 5.2: Operating conditions for determination of beryllium in coal slurries using uncoated tubes

(a) Spectrophotometer

Wavelength (nm):	234.9
Slit width (nm):	0.7
Lamp current (mA):	8
Background corrector:	On
Integration time (seconds):	8

(b) Furnace

Step	Temperature °C	Ramp (seconds)	Hold (seconds)	Internal argon flow (ml/min)
Dry 1	60	10	10	300
Dry 2	120	10	20	300
Ash	1000	20	20	300
Atomise	2700	0	6	50
Clean	2700	1	5	300

Table 5.3: Determination of beryllium in SARM coals

Sample	This work (a)	µgBe/g Certified
SARM 18	4.6 ± 0.20	4.1 (3.9 to 4.5)
SARM 19	3.3 ± 0.08	2.8 (2.3 to 3.1)
SARM 20	2.7 ± 0.07	2.5 (2.1 to 3.0)

(a) average of 4 determinations

The effect of magnesium nitrate ($Mg(NO_3)_2.6H_2O$) concentration on the response of an aqueous beryllium standard was studied . 15µl of a 0.004ppm standard (0.06ng Be) was injected into the tube. Differing volumes of a magnesium nitrate solution were added to the tube. The absorbance was measured and the curves illustrated in figure 5.2 plotted. Ashing was at 1400°C with atomisation at 2700°C. A minimum of about 10µg Mg (as magnesium nitrate) is needed to stabilise 0.06ng Be as indicated by the plateau on the curves. To ensure no ashing losses occurred, an excess of Mg was used and the matrix modifier was prepared by dissolving 10.5g of $(Mg(NO_3)_2.6H_2O$ in 1000ml water. This solution contained 1000ppm Mg, a 15µl aliqout thus containing 15µg Mg.

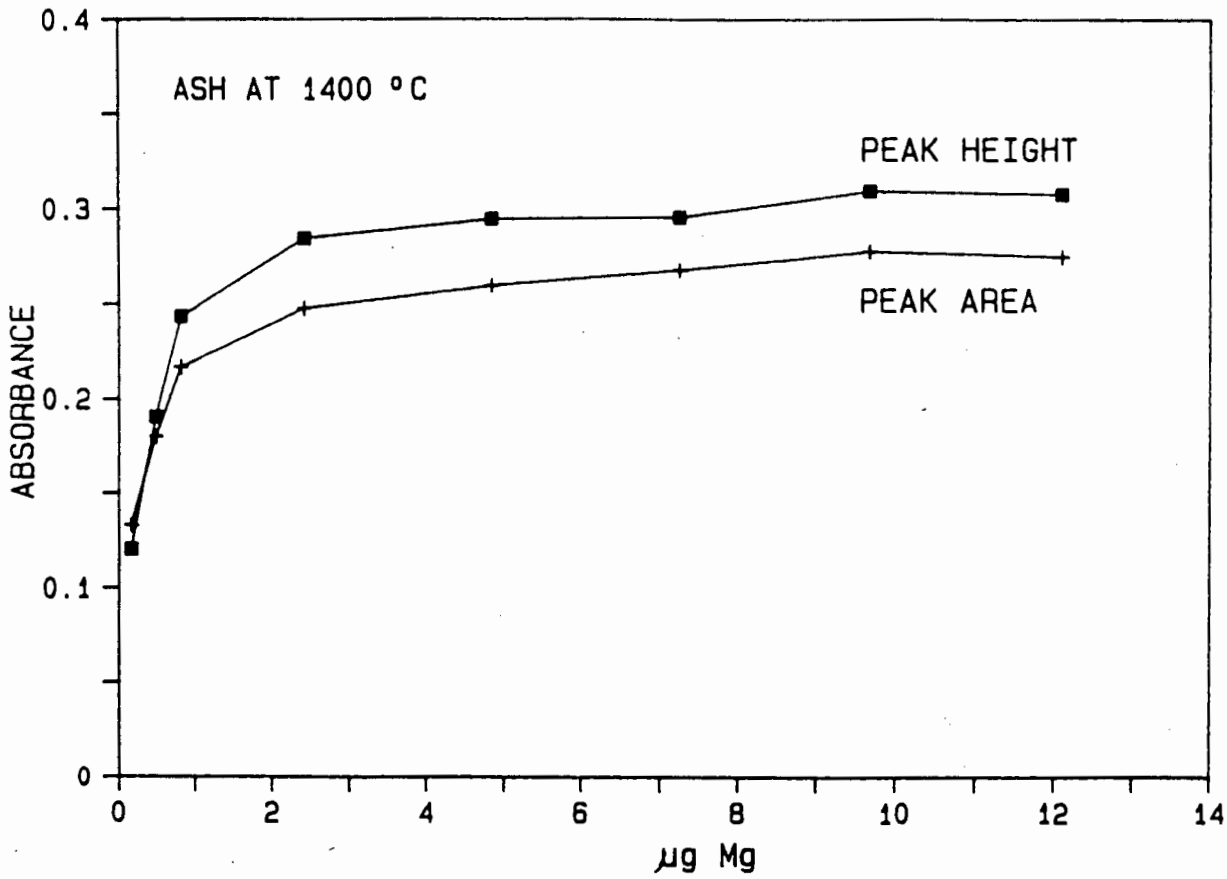


Figure 5.2: Effect of magnesium nitrate matrix modifier concentration on response of 0.06ng Be

The ashing curves of an aqueous Be standard and a SARM 20 coal slurry appear in figure 5.3. Ashing losses occur at temperatures in excess of 1600°C in the presence of the magnesium nitrate as indicated by the decrease of absorbance obtained at higher temperatures. The background absorbance of the slurry is low and well within the correction capability of the deuterium correction system.

It was then discovered that the response obtained depended on the history of the uncoated tube, as demonstrated by the experiment illustrated in figure 5.4.

Three solutions were prepared and injected in the sequence illustrated in the figure. Twenty-five atomisations of solution (ii) had been performed in the tube prior to the experiment. At the point labelled (a), ten replicate injections of solution (i) were made. At (b), six injections of solutions (i) plus (iii) were made, followed by five injections of (i) again, point (c). Solution (ii) was injected once (d), followed by four injections of solution (i), point (e). At (f), five injections of solutions (i) plus (iii) were made. A single injection of solution (ii) was made, point (g), followed by four injections of solutions (i) plus (iii), point (h).

The following hypothesis was proposed to explain the observed behaviour: Analysis of the coal slurry results in the formation of a thin layer of pyrolysed carbon due to the organic matter present in the coal, or to the formation of a metal carbide of one or more of the carbide forming elements in the coal. SARM 20 contains 17.66% silica [Rin84] and Runnels et al. [Run75] have shown that treatment of a graphite tube with silica results in beryllium peak enhancement by a factor of 7.3.

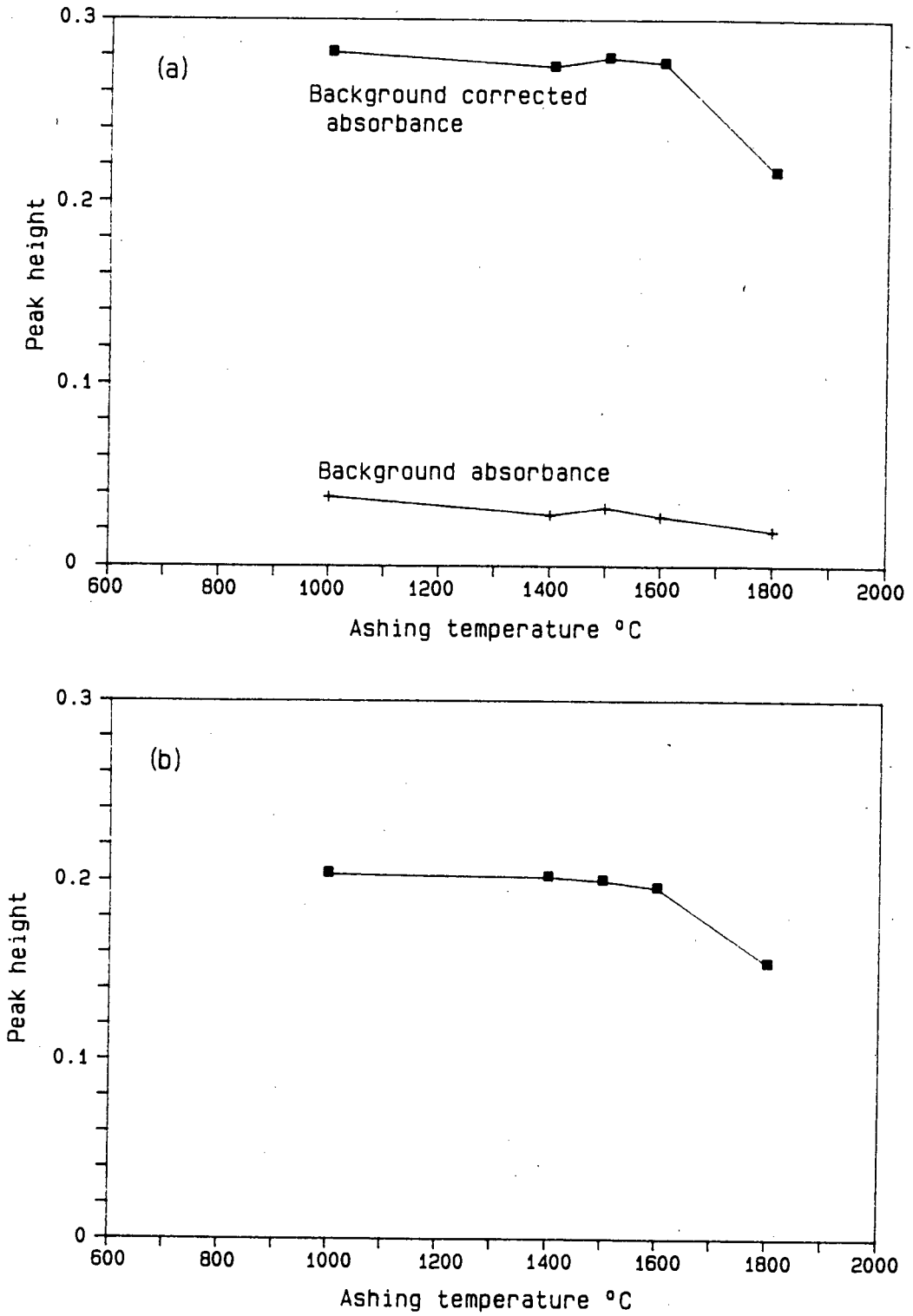


Figure 5.3: Optimisation of ashing temperature in magnesium nitrate modifier solution
(a) Coal slurry (22.9µg SARM 20)
(b) Aqueous Be standard (0.075ng Be)

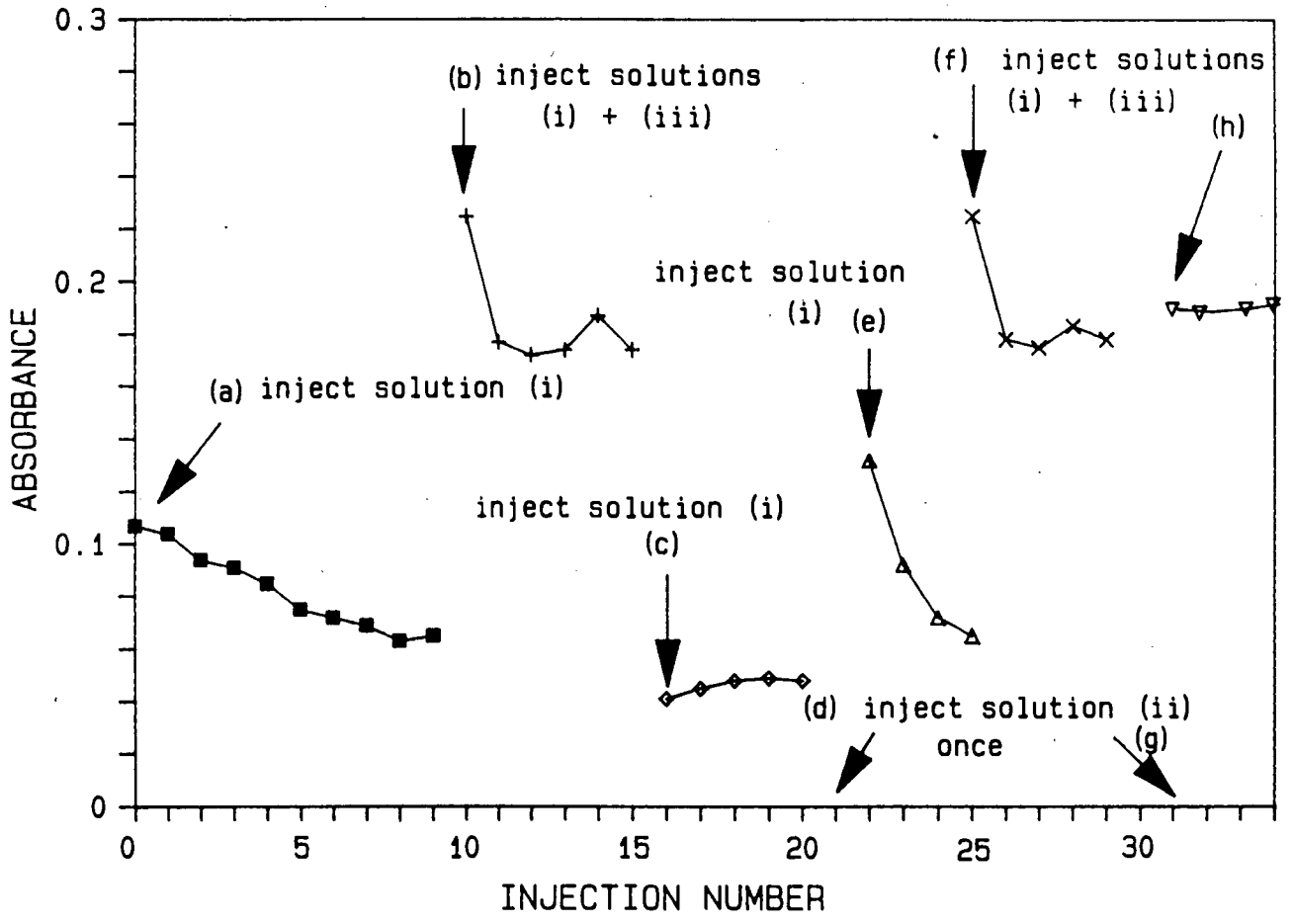


Figure 5.4: Response with uncoated tube

Key to solutions: (all in 0,005% (m/v) Triton X-100)
(i) 0.004ppm Be standard
(ii) SARM 20 slurry (0.0194g per 15ml)
(iii) 5% (v/v) ca. 65% nitric acid

20µl aliquots injected

At point (a), the layer is degraded by the successive atomisation of the Be aqueous standard, resulting in the decreasing absorbances observed due to the conditions for carbide formation becoming more favourable. Carbide formation competes with atomisation [Run75] and as the conditions for carbide formation become more dominant, the atomisation efficiency decreases resulting in a decreasing atomisation signal. Analysis of the Be aqueous standard in the presence of nitric acid results in the first reading being higher than the subsequent readings, as the residual beryllium carbide is decomposed or rendered unstable by the first addition of the acid. It is known that beryllium carbide is unstable in water [Run75]. The absorbance readings of the aqueous standard in the presence of nitric acid are higher than those in ~~the~~ its absence possibly due to the inhibition of the formation of diberyllium carbide.

At point (c), no pretreatment of the tube by the coal slurry occurred and absorbances are consistently depressed due to the formation of the diberyllium carbide complex. Runnels et al. [Run75] found that only 25% of beryllium is volatilised in an untreated furnace.

At point (d), a layer of pyrolysed carbon or metal carbide is once again formed by the pyrolysis of the coal, hence the enhanced absorbance observed by injecting the aqueous standard (e). Once again, the absorbances fall off in the subsequent injections. At (f) the beryllium carbide is once again dissolved. At (h), the first reading is not enhanced as no carbide formation occurred with injection of the coal slurry.

On the basis of this hypothesis, it can be concluded that injection of the coal slurry treats the tube in some way which inhibits carbide formation. The presence of nitric acid in the aqueous standard also yields conditions which

are unfavourable for carbide formation. In the real life analytical situation, the situation depicted in (g) and (h) occurs and the effects noted in the previous experiment will not be observed. A certain amount of carbide formation may still occur with the aqueous standard even in the presence of nitric acid which may explain the high results obtained for the analysis of the SARM coals.

The same trends were observed in the peak area mode indicating that the effects are not due to differences in atomisation rate, but rather to the total amount of absorbing beryllium atoms present. If injection of the coal slurry indeed leads to formation of a layer of pyrolysed carbon, atomisation of a fly ash slurry should not lead to the same effects due to the lower organic content of the fly ash (see table 4.2). If however, the behaviour is due to the formation of metal carbides atomisation of a fly ash slurry should lead to the same, or possibly more severe effect due to the higher concentration of carbide forming metals in fly ash compared to coal.

This hypothesis is not consistent with the study by Robbins et al. [Rob75] who encountered no problems with carbide formation. They noted that the Varian Techtron Model CRA-63 atomiser passes rapidly through the narrow stable carbide temperature range (1900 to 2200°C) so rapidly that no carbide formation problems occur. On the basis of this observation, no carbide formation problems should occur with the HGA-500 atomiser, especially with maximum power heating, as the temperature is ramped at a maximum rate from 1000°C (ashing step) to 2700°C (atomisation step). Runnels et al. [Run75] noted that beryllium carbide is not completely stable at 1950°C and slowly decomposes.

Further investigation into the mechanisms were not made as it was felt to be beyond the scope of the objectives of this

work. The use of the STPF approach for the analysis of slurried coal and fly ash was investigated.

5.2.2 Studies with platform atomisation

This approach was investigated for the determination of beryllium in slurried coal and fly ash samples. Initially the commercially available pyrolytic platforms were unavailable and "home-made" platforms, similar to the platforms described by Kaiser et al. [Kai81], were constructed [Pou85]. Pyrolytically coated graphite tubes were cut into small pieces (about 7 x 4mm) and inserted under the sample introduction port. These platforms were used for the determination of Be in NBS SRM 1633a after an acid digestion procedure using standard addition. No matrix modifier was used. The concentration of Be was found to be 12.5 ± 0.8µg/g (average of 3 determinations) which shows good agreement with the informational value of 12µg/g supplied by NBS. The "home-made" platforms were not suitable for routine analysis as problems were experienced with manually dispensing the samples on the platform reproducibly. The platforms tended to shift during sample introduction as the inside of the tube was not grooved. Furthermore, widely differing drying and ashing conditions were necessary for each individual platform, due to their differing geometry and position in the tube.

All further work was performed with platforms and tubes purchased from Perkin-Elmer.

The effectiveness of magnesium nitrate in stabilising Be at elevated ashing temperatures had been investigated in the previous work using uncoated graphite tubes. It is desirable to include nitric acid in the modifier solution to preserve the slurry samples and to avoid loss of analyte due to absorption to the container walls. Therefore the effect

of nitric acid concentration on the response of a coal and fly ash slurry, as well on an aqueous solution, was studied, figure 5.5. Nitric acid has little or no effect on the slurry response, but the aqueous standard shows a slightly enhanced absorbance in the presence of nitric acid.

The matrix modifier was prepared by dissolving 10.5g $(Mg(NO_3)_2.6H_2O$ in 0.005% (m/v) Triton X-100. 50ml concentrated nitric acid (ca.65%) was added and the solution diluted to 1000ml with the Triton X-100 solution.

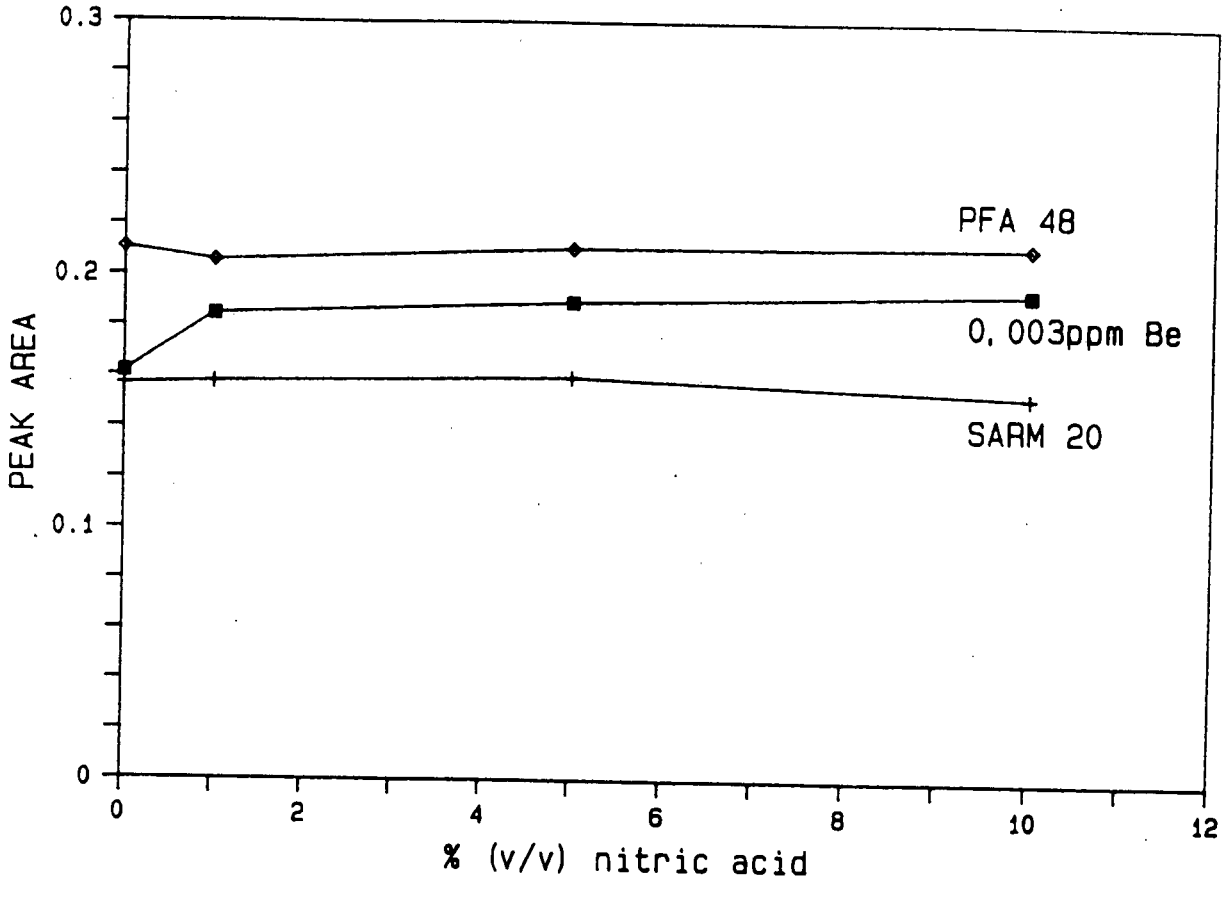


Figure 5.5: Effect of nitric acid concentration on response of coal slurry, fly ash slurry and aqueous standard

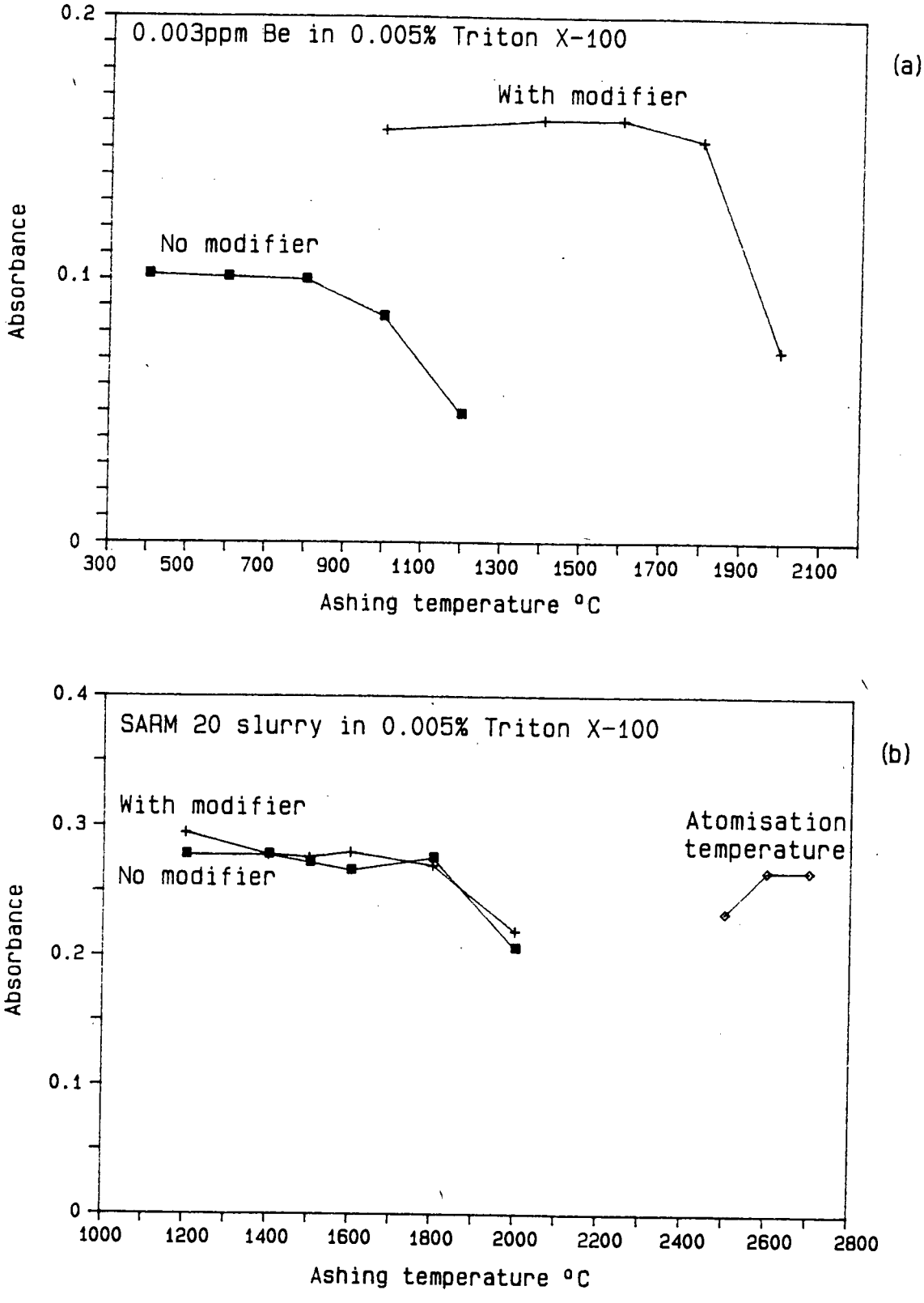


Figure 5.6: Optimisation of ashing and atomisation temperatures
(a) Aqueous standard
(b) Coal (SARM 20) slurry

5.2.2.1 Optimisation of ashing and atomisation temperatures

The response of a coal slurry and an aqueous beryllium standard in the matrix modifier solution and in 0.005% Triton X-100 solution is illustrated in figure 5.6. In the absence of matrix modifier, ashing losses from aqueous solution occurs at temperatures above about 800 °C, whereas in the presence of the modifier, losses occur above 1600°C (figure 5.6 (a)). The matrix modifier has little effect on the ashing profiles of the coal slurry, as the curves in the presence and absence of modifier are similar (figure 5.6 (b)) . The ashing curve of a fly ash slurry is illustrated in figure 5.7. An ashing temperature of 1600°C was therefor used for quantitative determinations.

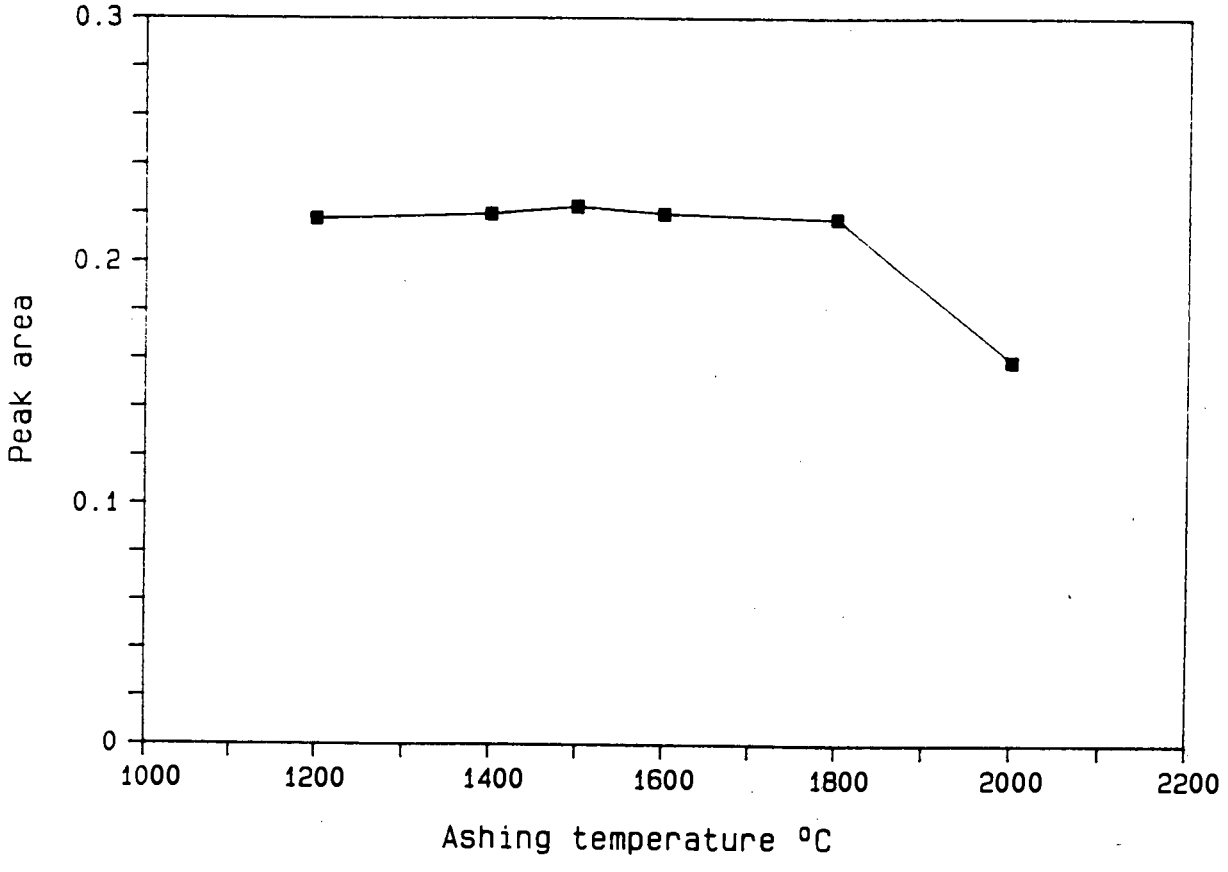


Figure 5.7: Optimisation of ashing temperature of fly ash (PFA 48) slurry in modifier solution

The atomisation curve of the coal slurry is illustrated in figure 5.6 (b). The peak areas at atomisation temperatures of 2600°C and 2700°C are approximately the same, but the peak height at 2700°C is higher than at 2600°C. At 2600°C the peak is noticeably wider, with a definite shoulder. This shoulder is more prominent at 2500°C. An atomisation temperature of 2700°C was therefore used.

5.3 RESULTS AND DISCUSSION

5.3.1 Performance of autosampler

The modified AS-40 autosampler described in Chapter 3 was used for all the beryllium determinations in slurried samples. Samples and aqueous standards (15ml) were placed in the glass vials described for automatic injection. The performance of the autosampler was investigated by atomising ten 20µl aliquots of an aqueous Be standard (0.003 µg/ml) and a slurry of SARM 20 (approximately 0.002 µg Be/ml). The relative standard deviation for the aqueous standard was 2.3% while that for the slurry was 3.3%. For coal samples particularly, a few particles tended to adhere to the outside of the capillary tubing, but this did not effect the precision of injections. The rinse cycle between injections was effective in eliminating cross contamination.

Several advantages were gained by the use of the autosampler. The most important was freedom from constant operator attendance at the instrument, thus allowing sample preparation to proceed during analysis. Convenient positioning of the balance, ultrasonic bath and all reagents needed for sample preparation is essential for operator comfort. More reproducible sample injection was achieved with the autosampler as the position of the capillary tip remained constant during analysis. With manual injection,

disturbance of the platform can occur, as well as poor reproducibility, especially with inexperienced operators.

5.3.2 **Linearity and detection limit**

Figure 5.8 illustrates a typical aqueous calibration graph for beryllium determinations. Excellent linearity to at least 45pg was obtained (r=1.0000). The detection limit (defined in section 4.5.3.1) was 0.7pg Be.

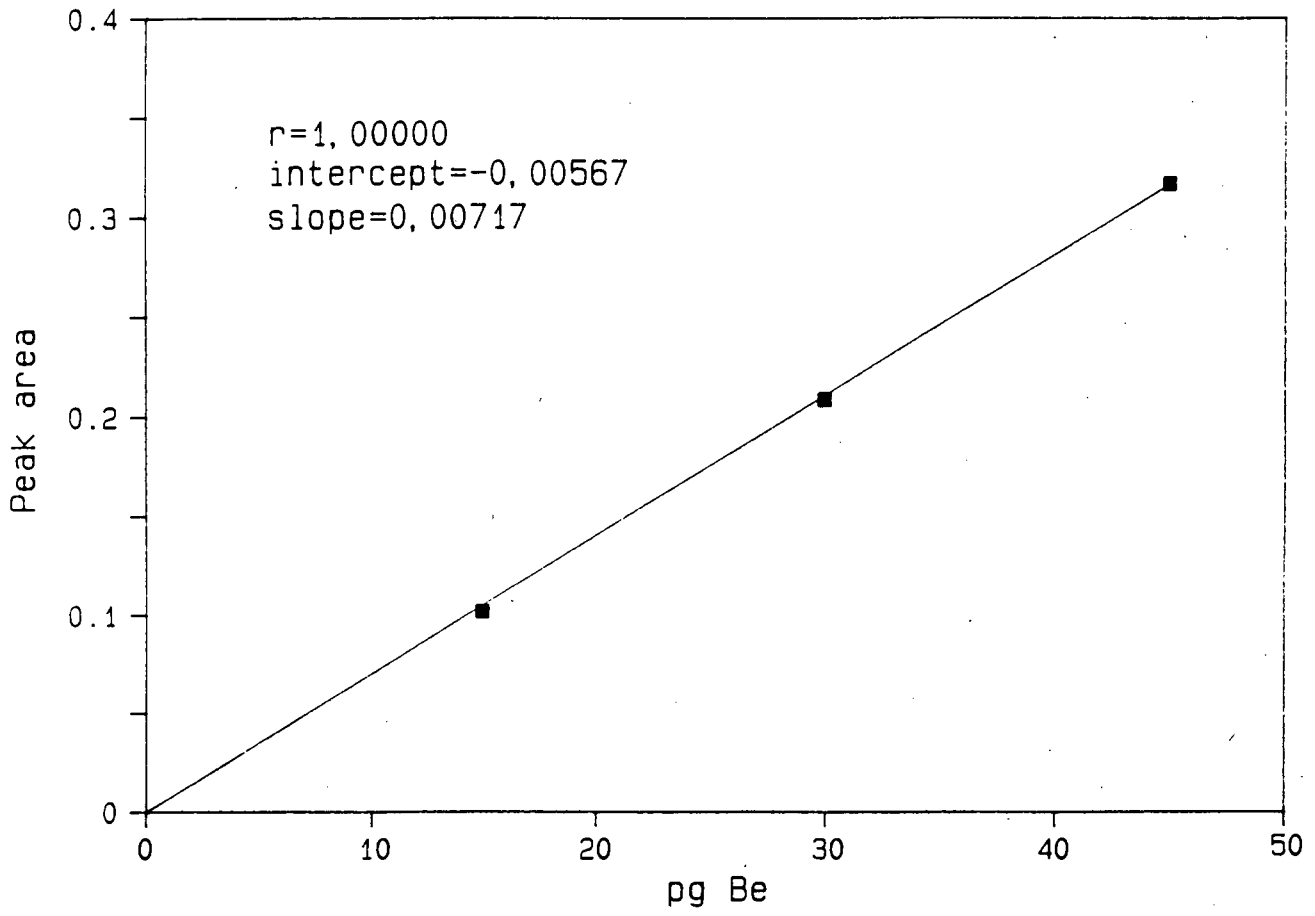


Figure 5.8: Calibration graph for Be determinations

5.3.3 Analysis of coal and fly ash samples

The results for the determination of Be in reference coal and fly ash standards are in Table 5.4. The accuracy was good as the results obtained compare well with the certified values. The precision (quoted as %RSD) was better than 11%.

Table 5.4: Determination of beryllium in reference coals and fly ash standards

Sample	Slurry analysis			Ceritified value µg Be/g
	Number of determin-ations	%RSD	Concentration µg Be/g	
SARM 18	8	6.9	4.1 ± 0.3	4.1 (3.9 - 4.5)
SARM 19	8	7.7	2.9 ± 0.2	2.8 (2.3 - 3.1)
SARM 20	6	4.2	2.4 ± 0.1	2.5 (2.1 - 3.0)
NBS SRM 1633a	5	10.7	11.6 ± 1.2	12[#]

[#] Value not certified, information only

Table 5.5 lists the results for the determination of beryllium in the South African coal samples. In all cases the concentration was greater than 1µg/g as noted by Vanhoe et al. [Van88]. The median concentration for beryllium in the coal samples investigated was 2.0 µg/g. The precision of determination (%RSD) is included for several samples and was generally better than 25%.

Table 5.5: Results for the determination of beryllium in South African coal samples

Sample	Origin	Number of determinations	% RSD	µg Be/g
PF 87	ARNOT BLR 4 COAL	4	8.7	1.4 ± 0.1
PF 88	CAMDEN BLR 4 COAL	2		2.0 ± 0.3
PF 89	CAMDEN BLR 6 COAL	4	14.4	1.9 ± 0.3
PF 90	DUVHA BLR 1 COAL	4	9.7	1.8 ± 0.2
PF 91	HENDRINA BLR 5 COAL	2		2.2 ± 0.1
PF 92	HENDRINA BLR 6 COAL	1		1.9
PF 93	KOMATI BLR 1 COAL	2		2.3 ± 0.2
PF 94	KOMATI BLR 2 COAL	1		2.7
PF 95	KOMATI BLR 6 COAL	4	10.5	2.4 ± 0.3
PF 96	KOMATI BLR 7 COAL	3	24.7	1.9 ± 0.5
PF 97	KOMATI BLR 8 COAL	3	14.7	2.6 ± 0.4
PF 98	KOMATI BLR 9 COAL	1		2.0
PF 99	KRIEL BLR 1 COAL	5	19.0	1.7 ± 0.3
PF 100	KRIEL BLR 6 COAL	2		2.1 ± 0.03
PF 101	MATLA BLR 1 COAL	2		1.8 ± 0.4
PF 102	WILGE BLR 6 COAL	2		2.0 ± 0.2
PF 103	WILGE BLR 9 COAL	3	19.8	2.1 ± 0.4

The results for the analysis of the South African fly ash samples appear in table 5.6. Several samples were analysed by an acid digested procedure followed by GFAAS and are included in the table. The results obtained with a digestion procedure and ICP-AES procedure [Pou85] are also included. Most of the fly ash results showed reasonable agreement (within 22%) with the values obtained by the digestion procedure, with the exception of PFA 53 and 57. Both these samples were from the Matla Power Station boiler 1. The result obtained for PFA 53 agrees well with that of PFA 45, which are the RH1 and LH1 precipitators respectively. Similarly PFA 57 agrees well with PFA 49, which are the RH5 and LH5 precipitators respectively. The RSD was better than 10%. The median concentration was 5.8µg/g.

Table 5.6: Results for beryllium in South African fly ash samples

Sample	Origin	Slurry analysis		Digestion procedure	
		% RSD	µg Be/g	ICP (Pou85) µg Be/g	GFAAS µg Be/g
PFA 4	ARNOT BLR 4 PFA LH2 PR		5.3 ± 0.1 (a)	5.6	5.7 ± 0.9 (d)
PFA 13	CAMDEN BLR 6 PFA LH2 PR	4.1	11.3 ± 0.5 (b)	11.3	12.0
PFA 21	DUVHA BLR 1 PFA RH ROW 1 PR		3.5		
PFA 22	DUVHA BLR 1 PFA RH ROW 2 PR	4.0	6.0 ± 0.2 (b)		
PFA 23	DUVHA BLR 1 PFA RH ROW 3 PR	0.4	8.1 ± 0.03 (b)		
PFA 45	MATLA BLR 1 PFA LH1 PR	5.0	4.8 ± 0.2 (c)	5.6	5.7 ± 0.5 (e)
PFA 46	MATLA BLR 1 PFA LH2 PR		5.2		5.8 ± 0.6 (c)
PFA 48	MATLA BLR 1 PFA LH4 PR		8.1 ± 0.2 (a)	8.0	7.9 ± 1.0 (a)
PFA 49	MATLA BLR 1 PFA LH5 PR	10.0	4.4 ± 0.4 (b)	5.5	
PFA 50	MATLA BLR 1 PFA LH6 PR		6.2		6.5
PFA 53	MATLA BLR 1 PFA RH1 PR		4.6	6.7	
PFA 56	MATLA BLR 1 PFA RH4 PR	4.5	7.0 ± 0.3 (b)		
PFA 57	MATLA BLR 1 PFA RH5 PR		4.2	7.3	
PFA 58	MATLA BLR 1 PFA RH6 PR		5.6 ± 0.02 (a)	6.8	
PFA 59	MATLA BLR 1 PFA RH7 PR	4.9	6.4 ± 0.3 (c)	7.0	
PFA 66	MATLA TEST 2 PFA RH1 PR	2.8	4.7 ± 0.1 (b)	6.0	
PFA 68	MATLA TEST 2 PFA RH3 PR	3.5	7.2 ± 0.3 (b)	8.7	
PFA 69	MATLA TEST 2 PFA RH4 PR		8.1 ± 0.4 (a)	9.2	

(a) average of 2 determinations
(b) average of 3 determinations
(c) average of 4 determinations
(d) average of 5 determinations
(e) average of 6 determinations

The injection precision for several coal and fly ash samples appear in table 5.7. The precision for the fly ash is generally better than for the coal. This is probably due to the particle size effects discussed in section 3.7.3.

Table 5.7: Injection precision for beryllium determinations

Sample	Description	%RSD*
SARM 20		5.0
NBS SRM 1633a		13.8
PF 90	CAMDEN BLR 6 COAL	8.0
PF 95	KOMATI BLR 6 COAL	4.2
PF 96	KOMATI BLR 7 COAL	13.6
PF 99	KRIEL BLR 1 COAL	12.1
PF 103	WILGE BLR 9 COAL	6.2
PFA 13	CAMDEN BLR 6 PFA LH2 PR	1.6
PFA 21	DUVHA BLR 1 PFA RH ROW 1 PR	5.2
PFA 22	DUVHA BLR 1 PFA RH ROW 2 PR	6.8
PFA 23	DUVHA BLR 1 PFA RH ROW 3 PR	3.5
PFA 45	MATLA BLR 1 PFA LH1 PR	5.8
PFA 49	MATLA BLR 1 PFA LH5 PR	7.3
PFA 56	MATLA BLR 1 PFA RH4 PR	5.2
PFA 59	MATLA BLR 1 PFA RH7 PR	6.2
PFA 66	MATLA TEST 2 PFA RH1 PR	4.8
PFA 68	MATLA TEST 2 PFA RH3 PR	1.8

* Average of 5 injections

The results for the coal and fly ash samples are depicted graphically in figure 5.9 (Duvha, Arnot and Camden samples) and figure 5.10 (Matla samples). In all cases, beryllium levels in the fly ash are greater than in the corresponding coal. A general trend of increasing beryllium concentration with consecutive precipitators was noted with the Duvha samples, as was observed with cadmium (section 5.4.3.2) and by for the elements studied by Willis [Wil82].

Using the available results, enrichment of beryllium in the fly ash relative to the corresponding coal was calculated. The Matla boiler 1 coal has an ash content of 24.4% [Wil82] and the fly ash in the LH4 precipitator is enriched 1.1 times. An enrichment factor of 3.9 was calculated for cadmium. No enrichment of the Arnot LH2 fly ash was found, which is consistent with the observation for cadmium.

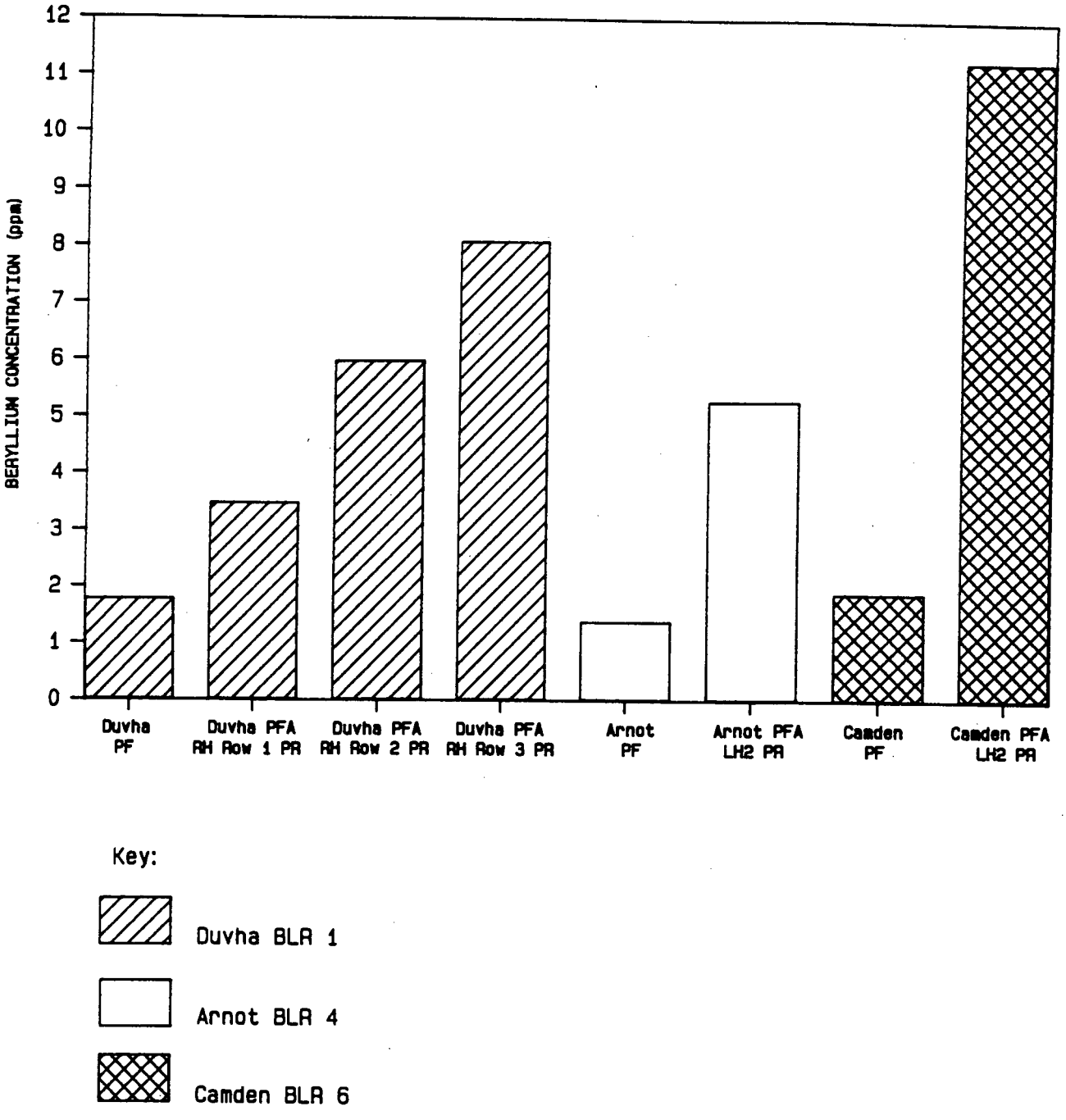


Figure 5.9: Beryllium concentration in Duvha, Arnot and Camden coals and fly ashes

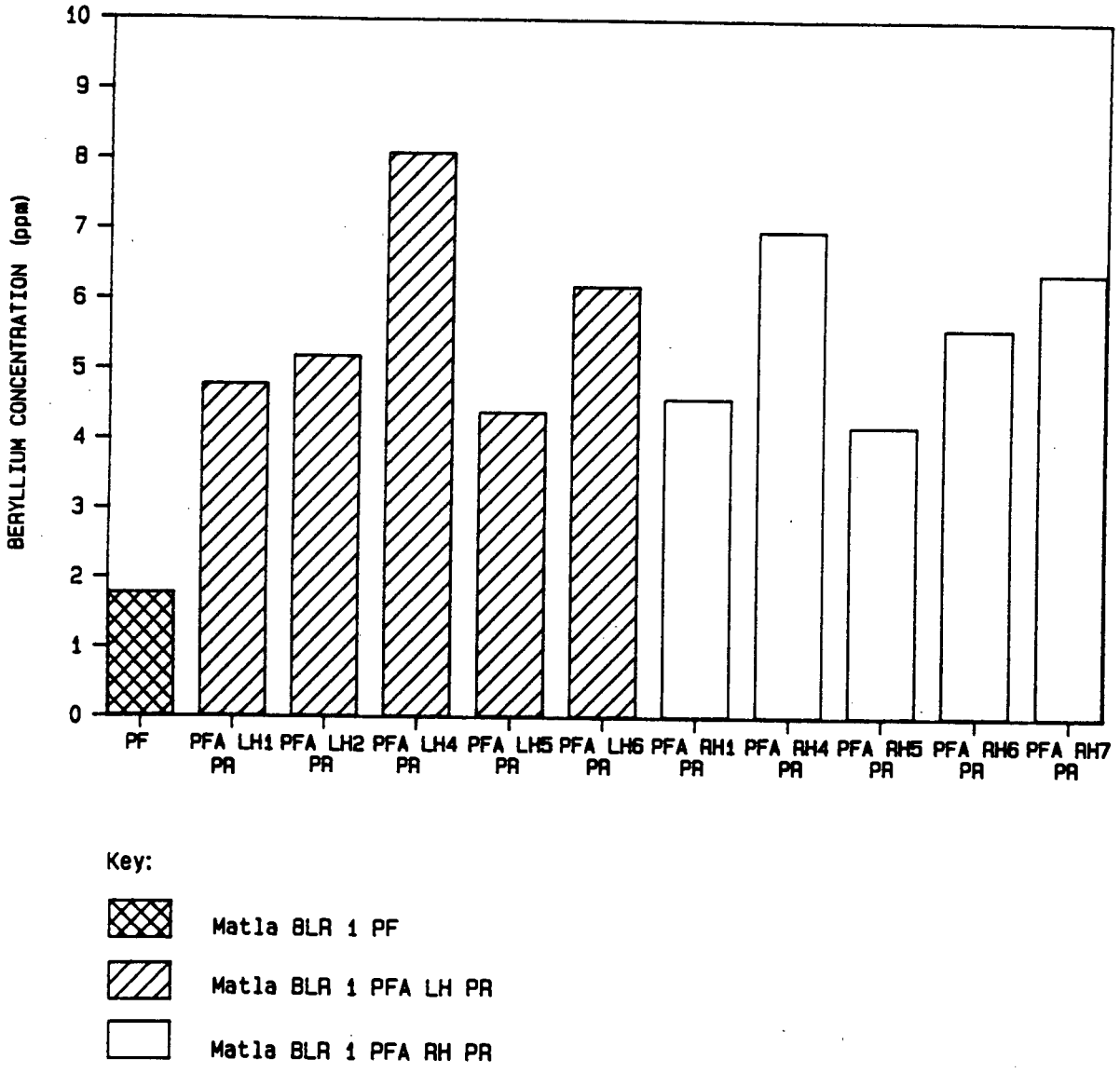
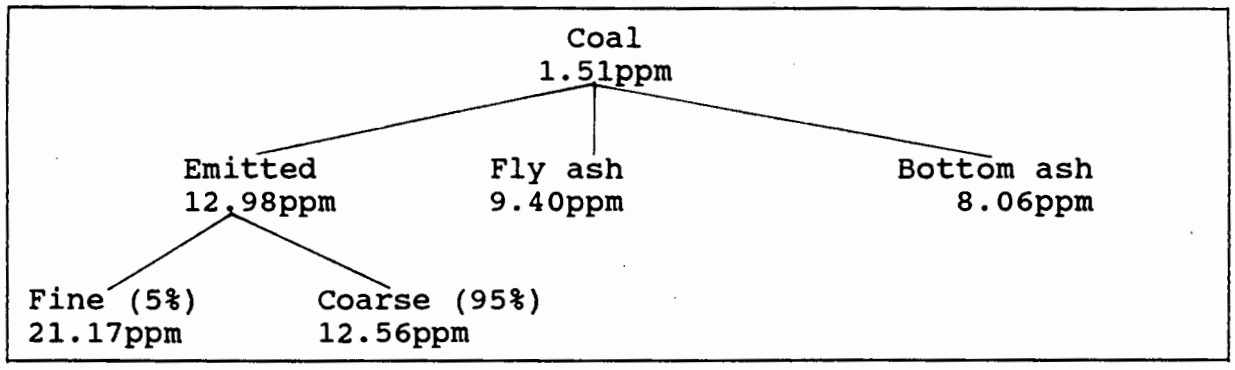


Figure 5.10: Beryllium concentration in Matla coal and fly ashes

Vanhoe et al. [Van88] did a mass balance study of beryllium in a coal-fired power plant. Beryllium was determined in the coal, bottom ash, fly ash and the emitted particulate matter. Their results were as follows:



They concluded that the bottom ash and fly ash are not enriched in beryllium if the 17% ash content of the coal is considered. Beryllium is slightly enriched in the particulate matter. Most of the beryllium is collected in the fly ash, whereas 2.1% is emitted.

Approximately 35 dried, ground samples could be determined in a 8.5 hour day with a single tube and platform (about 200 firings). With coal samples, a residue was observed on the platform, the excessive build up of which was indicated by multiple peaks, erratic atomisation and obstruction of the beam. Manual removal of the residue was occasionally necessary (about once a day) and effectively eliminated the problem.

5.4 CONCLUSIONS

An analytical procedure for the determination of beryllium in coal and fly ashes was developed. The procedure utilises platform atomisation with magnesium nitrate matrix modification and automatic sample introduction.

Calibration is with aqueous standards and the results are calculated with peak area measurements. A single method is used for both coal and fly ash samples.

The accuracy of the method was evaluated by analysing standard reference materials and by comparison with acid digested samples analysed by GFAAS and ICP-AES. The precision was evaluated by replicate analyses of the same sample. Acceptable accuracy and precision was obtained.

6

DISCUSSION AND CONCLUSION

6.1 SAMPLE INTRODUCTION

The direct analysis of coal and fly ash was achieved by introducing slurried samples into the graphite furnace. This method of sample introduction was preferred to the introduction of the solid, finely powdered sample for the following reasons:

1. No need for mass determination for each individual analysis as a fixed volume of slurry is injected.
2. Less manipulation is required for sample introduction thus reducing risks of sample introduction losses.
3. No need for separate injection of matrix modifiers or other reagents as the slurry is prepared in a solution of the necessary chemicals, ie. with the slurry method a single injection suffices.
4. Less work is required for analysis which is especially important in routine industrial applications where large numbers of samples have to be analysed. Operator comfort is greater which reduces the risks of the production of unreliable data obtained by stressed analysts.
5. The procedure simulates that followed for the conventional analysis of liquid samples which may make acceptance of the technique easier for routine applications. Standard automatic liquid pipettes, which are common to most laboratories, can be utilised.
6. Sample introduction is more amenable to automation.

In certain instances, direct analysis of powder samples are

preferred, these are:

1. For determinations when limited sample amounts are available.
2. For homogeneity studies of solid samples.
3. When very low concentrations have to be determined as there is an upper limit to the slurry concentration which can be successfully and reproducibly injected.

Automatic sample introduction was achieved and was the first slurry autosampler utilising magnetic stirring reported in the literature [Har89]. The advantages gained by use of the autosampler were:

1. Freedom from constant operator attendance at the Atomic Absorption instrument, thus allowing for more effective time-utilisation.
2. Improved reproducibility of injections. With manual injection, especially with inexperienced operators, poor reproducibility and disturbance of the platform can occur.

Utilisation of the semi-automatic autosampler in conjunction with a printer allowed for unattended analysis of a single sample. The main disadvantage of this autosampler was the requirement for manually replacing the sample container in the tray. This was overcome by the design and construction of a fully automatic autosampling unit. This unit allows for unattended analysis from 14 sample containers.

Both units utilise simple magnetic stirring for the maintenance of homogenous slurries during sampling. Little modification to the standard autosampler is required and switch over to liquid sampling is achieved in under 5

minutes. These units are inexpensive and can easily be constructed in a standard workshop.

6.2 DEVELOPMENT AND EVALUATION OF ANALYTICAL PROCEDURES

Analytical procedures were developed for the determination of cadmium and beryllium in coal and fly ash. Minimal sample manipulation was required as sample preparation simply involved grinding for two hours and slurrying in a suitable solvent. Calibration for both the cadmium and beryllium determinations were with calibration graphs constructed with aqueous standards. The technique of matrix modification was applied and a single procedure for the analysis of coal and fly ash for cadmium or beryllium was used. Cadmium could be determined with pyrolytically coated graphite tubes but platform atomisation was necessary for the beryllium determinations.

Langhmyhr, in his review of direct solid analysis in Atomic Spectroscopy [Lan85/2] commented that

"Relative standard deviations of 5-10% are frequently obtained for elements present at the 1 ppm level; similarly, at the 1 ppb level, values in the range 10-30% have to be considered as normal. These figures compare favourably with those of other methods for the determination of trace elements".

Acceptable precision was obtained in this work. The median concentration of cadmium in coal was 0.05μg/g and the precision (%RSD) was generally better than 30%. For fly ash, at a median concentration of 0.12μg/g, the precision was generally better than 10%. The median concentration of beryllium in coal was 2μg/g and the precision better than 25%, with RSD values of 10-15% regularly obtained. In fly ash, at a median concentration of 5.8μg/g the precision was better than 10%, with typical RSD values of 3-5%.

The methods were found to be accurate as good agreement was obtained with solid reference standard certified values and/or with alternative analytical procedures.

When evaluating analytical method performance, the criteria for evaluation will depend on the nature of the results required. For certain applications, quick screening methods suffice, whereas other applications demand a high degree of accuracy and precision. Esser [Ess87], in his publication dealing with solid sampling in industrial product control, rated accuracy and precision secondary to reliability and fast data output for industrial applications. The applicability of the methods developed in this work will depend not only on precision and accuracy criteria, but on other factors as well.

Shorter sample preparation times were required for the slurry methods in comparison to the high pressure bomb procedure. In this work, reduction of sample particle size constituted the major fraction of the total analysis procedure, as two hours grinding in a ball mill was necessary. This can be shortened considerably by employing more efficient grinding apparatus such as the swing mill. Sample grinding is also required for the bomb method to ensure that a representative aliquot is taken for analysis. However, with the slurry method, no digestion time is required, whereas approximately 4 hours heating is required for the bomb method. The slurry method requires fewer expensive reagents such as high purity hydrofluoric acid and a cost saving advantage in terms of reagents as well as analytical time is gained.

6.3 APPLICATION OF ANALYTICAL PROCEDURES

The analytical procedures were applied to the analysis of South African coal and fly ash samples. A few trends were

noted with the available data, namely, increasing cadmium and beryllium concentrations in fly ash from consecutive precipitators from several power stations and enrichment of cadmium in fly ash collected from the Duvha and Matla power stations. However, no attempt was made to do an in-depth study of enrichment effects or trace-elemental mass balance studies. The results obtained indicate that the methods could be applied to obtain such data.

The methods could be utilised by relatively unskilled personnel provided that adequate training on the principles involved is provided. As with most analytical procedures, the success of routine application depends upon, amongst other factors, the in-depth characterisation of all the steps constituting the procedure.

6.4 FURTHER STUDIES

Several interesting effects were noted during method development. The first of these was the peak enhancement obtained when ashing coal slurries in the presence of oxygen. The second effect was the peak enhancement noted with beryllium aqueous standards with uncoated tubes after prior atomisation of a coal sample. Coal is a highly complex matrix and the reactions occurring in the tube, especially in a reactive atmosphere of oxygen, are likely to be complex. A detailed study of the reactions may lead to an improvement of knowledge of the mechanisms occurring with the direct analysis of complex samples.

6.5 CONCLUDING REMARKS

The direct analysis of slurried coal and fly ash was achieved using relatively unsophisticated equipment. Several studies [Wel86, Let87] have shown that certain spectral interferences obtained with deuterium arc

background correction (the system used in this work) can be eliminated or removed by the use of more sophisticated systems such as Zeeman-effect. Use of computerised state-of-the-art data manipulation/acquisition systems could facilitate method development and data processing. Appearance temperatures could be monitored as well as allowing the application of more sophisticated integration and data manipulation techniques.

The technique of direct solid analysis was successfully applied to the determination of trace levels of cadmium and beryllium in coal and fly ash.

REFERENCES

REFERENCES

A

ANN83: H.J. Annegarn, A.C.D. Leslie, J.W. Winchester and J.P.F. Sellschop, Aerosol Science and Technology, 1983, **2**, 489.

ATS87: I. Atsuya, K. Itohand and K. Atatsuka, Fresenius' Z. Anal. Chem., 1987, **328(4-5)**, 338.

B

BAU85: M. Baucells, G. Lacort and M. Roura, Analyst, 1985, **110**, 1423.

BEA80: M. Beaty, W. Barnett and Z. Grobenski, Atomic Spectrosc., 1980, **1(3)**, 72.

BET83: M. Bettinelli, At. Spectrosc., 1983, **4(1)**, 5.

BET86: M. Bettinelli, N. Pastorelli and U. Baroni, At. Spectrosc., 1986, **7(2)**, 45.

BET88: M. Bettinelli, U. Baroni and N. Pastorelli, J. Anal. Atom. Spectrom., 1988, **3(7)**, 1005.

BRO84: R.F. Browner and A.W. Boorn, Anal. Chem., 1984, **56(7)**, 786A.

BRO87: A.A. Brown, M. Lee, G. Kullemer and A. Rosopulo, Fresenius' Z. Anal. Chem., 1987, **328**, 354.

C

CAM78: E.Y. Campbell and F.O. Simon, Talanta, 1978, **25**, 251.

CHA80: C.L. Chakrabarti, C.C. Wan and W.C. Li, Spectrochim. Acta, 1980, **35B**, 93.

D

DAV74: R.L. Davison, D.F.S. Natusch, J.R. Wallace, C.A. Evans, Environ. Sci. Technol., 1974, **8(13)**, 1107.

DEK87: A.M. De Kersabiec and M. Benedetti, Fresenius' Z. Anal. Chem., 1987, **328(4-5)**, 342.

DUE87: R. Duernberger, P. Esser and A. Janssen, Fresenius' Z. Anal. Chem., 1987, **327(3-4)**, 343.

E

EAT83: D.K. Eaton and J.A. Holcombe, Anal. Chem., 1983, **55**, 946.

EBD82: L. Ebdon and M.R. Cave, Analyst, 1982, **107**, 172.

EBD82/2: L. Ebdon and W.C. Pearce, Analyst, 1982, **107**, 942.

EBD87: L. Ebdon and A. Lechotycki, Microchem. J., 1987, **36**, 207.

EBD87/2: L. Ebdon and J.R. Wilkinson, J. Anal. At. Spectrom., 1987, **2**, 39.

EBD87/3: L.Ebdon and H.G.M. Parry, 1987, J. Anal. At. Spectrom., 1987, **2**, 131.

EBD87/4: L. Ebdon and J.R. Wilkinson, J. Anal. At. Spectrom., 1987, **2**, 325.

EBD88: L. Ebdon and H.G.M. Parry, J. Anal. At. Spectrom., 1988, **3**, 131.

EDI75: R.D. Ediger, At. Absorption Newlett., 1975, **14**, 127.

ELL88: W.G. Ellis, V.F. Hodge, D.A. Darby, C.L. Jones and T.A. Hinners, At. Spectrosc., 1988, **9(6)**, 181.

EPS89: M.S. Epstein, G.R. Carnrick, W. Slavin and N.J. Miller-Ihli, Anal. Chem., 1989, **61**, 1414.

ESS87: P. Esser, Fresenius' Z. Anal. Chem., 1987, **32B**, 410.

F

FER81: F.J. Fernandez, M.M. Beaty and W.B. Barnett, At. Spectrosc., 1981, **2(1)**, 16-21.

FIS78: G.L. Fisher, B.A. Prentice, D. Silberman, T.M. Ondov, A.H. Bierman, R.C. Ragaini and A.R. McFarland, Environ. Sci. Technol., 1978, **12**, 447.

FRE77: W. Frech and A. Cedergren, Anal. Chim. Acta, 1977, **88**, 57.

FRE85: W. Frech, E. Lundberg and A. Cedergren, Prog. analyt. atom. Spectrosc., 1985, **8**, 257.

FRY77: R.C. Fry and M.B. Denton, Anal. Chem., 1977, **49(9)**, 1413.

FUL77: C.W. Fuller and I. Thompson, Analyst, 1977, **102**, 141.

FUL81: C.W. Fuller, R.C. Hutton and B. Preston, Analyst, 1981, **106(1266)**, 913.

FUL83: M.H. Fulekar, D.S. Naik and J.M. Dave, Intern. J. Environmental Studies, 1983, **21**, 179.

FUL87: C.W. Fuller, Anal. Proc., 1987, **24**, 246.

G

GEL79: P. Geladi and F. Adams, Anal. Chim. Acta, 1979, **105**, 219.

GIL62: P.T. Gilbert, Anal. Chem , 1962, 34, 1025.

GLA77: E.S. Gladney, At. Absorp. Newslett., 1977, **16(2)**, 42.

GOV71: K. Govindaraju, G. Mevelle and C. Chouard, Chem. Geol., 1971, **8**, 131.

GRO81: Z. Grobenski, R. Lehmann and B. Welz, Atomic Spectroscopy Application Study No. 667, 1981.

GRO82: Z. Grobenski, R. Lehmann, R. Tamm and B. Welz, Mikrochim. Acta (Wien), 1982, **1**, 115.

GUE80: R. Guevremont, Anal. Chem., 1980, **52**, 1574.

H

HAR71: W.W. Harrison and P.O. Juliano, Anal. Chem., 1971, **43(2)**, 248.

HAR73: A.M. Hartstein, R.W. Freedman and D.W. Platter, Anal. Chem., 1973, **45(3)**, 611.

HAR89: L. Haraldsen and M.A.B. Pougnet, Analyst, 1989, **114**, 1331.

HEA80: J.B. Headridge, Spectrochim. Acta, 1980, **35B**, 785.

HEA82: J.B. Headridge and R.A. Nicholson, Analyst, 1982, **107**, 1200.

HER85: R.F.M. Herber, A.M. Roelofsen, W.H. Roelfzema and J.H.J.C. Peereboom-Stegeman, Fresenius' Z. Anal. Chem., 1985, **322**, 743.

HIN85: M.W. Hinds, K.W. Jackson and A.P. Newman, Analyst, 1985, **110**, 947.

HIN88: M.W. Hinds, M. Katyal and K.W. Jackson, J. Anal. At. Spectrom., 1988, **3**, 83.

J

JAC83: K.W. Jackson and A.P. Newman, Analyst, 1983, **108**, 261.

K

KAI81: M.L. Kaiser, S.R. Koirtyohann, E.J. Hinderberger and H.E. Taylor, Spectrochim. Acta, 1981, **36B**, 773.

KOR76: J. Korkisch and A. Sorio, Anal. Chim. Acta, 1976, **82**, 311.

KOR76/2: J. Korkisch, A. Sorio and I. Steffan, Talanta, 1976, **23**, 289.

KUR85: U. Kurfürst, Fresenius' Z. Anal. Chem., 1985, **322**, 660.

KUR87: U. Kurfürst, Fresenius' Z. Anal. Chem., 1987, **328**, 316.

L

LAN76: F.J. Langmyhr and J. Aamodt, Anal. Chim. Acta, 1976, **87**, 483.

LAN80: F.J. Langmyhr and U. Aadalen, Anal. Chim. Acta, 1980, **115**, 365.

LAN85: F.J. Langmyhr and G. Wibetoe, Prog. analyt. atom. Spectrosc., 1985, **8**, 193.

LAN85/2: F.J. Langmyhr, Fresenius' Z. Anal. Chem., 1985, **322**, 654.

LET87: V.A. Letourneau, B.M. Joshi and L.C. Butler, At. Spectrosc., 1987, **8(5)**, 145.

LUN79: E. Lundberg, W. Frech, Anal. Chim. Acta, 1979, **104**, 75.

LUN79/2: E. Lundberg, W. Frech, Anal. Chim. Acta, 1979, **108**, 75.

LVO78: B.V L'Vov, Spectrochim. Acta, 1978, **33B**, 153.

M

MAE78: F.J.M.J. Maessen, I. Balke and R. Massee, Spectrochim. Acta, 1978, **33B**, 311.

MAN83: D.C. Manning and W. Slavin, Appl. Spectrosc., 1983, **37(1)**, 1.

MAT81: J.P. Matousek, Prog. analyt. atom. Spectrosc., 1981, **4**, 247.

MIL88: N. J. Miller-Ihli, J. Anal. At. Spectrom., 1988, **3**, 73.

N

NAD80: R.A. Nadkarni, Anal. Chem., 1980, **52**, 929.

NAK88: T. Nakamura, K. Okubo and J. Sato, Anal. Chim. Acta, 1988, **209(1-2)**, 287.

NAR84: H.D. Narres, C. Mohl and M. Stoeppler, Intern. J. Environ. Anal. Chem., 1984, **18**, 267.

NAT74: D.F.S. Natusch and J.R. Wallace, Science, 1974, **183**, 202.

NIC78: J.A. Nichols, R.D. Jones and R. Woodriff, Anal. Chem., 1978, **50(14)**, 2071.

O

ORE77: J.E. O'Reilly and M.A. Hale, Anal. Lett., 1977, **10(13)**, 1095.

ORE79: J.E. O'Reilly and D.G. Hicks, Anal. Chem., 1979, **51(12)**, 1905.

ORR85: M.J. Orren, L.C. Haraldsen and M.A.B. Pougnet, Paper presented at "Analytical Chemistry in the exploration, mining and processing of material", Second International Symposium, South Africa, 15-19 April 1985

P

POU85: M.A.B. Pougnet, M.J. Orren and L. Haraldsen, Intern. J. Environ. Anal. Chem., 1985, **21**, 213.

R

RET86: T.M. Rettberg and J.A. Holcombe, Anal. Chem., 1986, **58**, 1462.

RIN84: E.J. Ring and R.G. Hansen, Mintek Report No. M169, 21 December 1984.

ROB75: W.K. Robbins, J.H. Runnels and R. Merryfield, Anal. Chem., 1975, **47(13)**, 2095.

RUN75: J.H. Runnels, R. Merryfield and H.B. Fisher, Anal. Chem., 1975, **47(8)**, 1258.

S

SAL82: S.G. Salmon and J.A. Holcombe, Anal. Chem., 1982, **54**, 630.

SCH87: G. Schlemmer and B. Welz, Fresenius' Z. Anal. Chem., 1987, **328**, 405.

SCH88: W.F. Schmidt, and F. Dietl, Fresenius' Z. Anal. Chem., 1988, **329(8)**, 853.

SHA89: X.-Q. Shan, Z. Yian and Z.-M. Ni, Anal. Chim. Acta, 1989, **217**, 271.

SIE73: D.D. Siemer , J.F. Lech and R. Woodriff, Spectrochim. Acta, 1973, **28B**, 469.

SIE74: D.D. Siemer and R. Woodriff, Spectrochim. Acta, 1974, **29B**, 269.

SLA83: W. Slavin, G.R. Carnrick, D.C. Manning and E. Pruszkovska, At. Spectrosc., 1983, **4**, 69.

STE85: S.C. Stephen, D. Littlejohn and J.M. Ottaway, Analyst, 1985, **110**, 1147.

STE87: S.C. Stephen, J.M. Ottaway and D. Littlejohn, Fresenius' Z. Anal. Chem., 1987, **328**, 346.

STO86: M. Stoeppler, Intern. J. Environ. Anal. Chem., 1986, **27**, 231.

STR87: G. Strübel, V Rzepka-Glinder, and K.H. Grobecker, Fresenius' Z. Anal. Chem., 1987, **328**, 382.

STU82: A. Stupar and R. Ajlec, Analyst, 1982, **107**, 144.

STY87: D.L. Styris and D.A. Redfield, Anal. Chem., 1987, **59**, 2897.

T

TAL72: Y. Talmi and G.H. Morrison, Anal. Chem., 1972, **44(8)**, 1455.

TAL74: Y. Talmi, Anal. Chem., 1974, **46(8)**, 1005.

THO75: K.C. Thompson, R.G. Godden and D.R. Thomerson, Anal. Chim. Acta, 1975, **74**, 289.

V

VAN80: J.C. van Loon, Anal. Chem., 1980, **52(8)**, 955A.

VAN88 H. Vanhoe, C. Vandecasteele, B. Desmet and R. Dams, J. Anal. Atom. Spectrom., 1988, **3**, 703.

VES77: O. Vesterberg and T. Bergstrøm, Clin. Chem., 1977 **232**, 555.

VÖL85: U. Völlkopf, Z. Grobenski, R. Tamm and B. Welz, Analyst, 1985, **110**, 573.

W

WAT82: R.J. Watling and H.R. Watling, S. Afr. J of Science, 1982, **78**, 164.

WAT86: A.E. Watson, S. Afr. J. Chem., 1986, **39**(3), 147.

WEL86: B. Welz and G. Schlemmer, J. Anal. At. Spectrom., 1986, **1**, 119.

WIL75: J.B. Willis, Anal. Chem., 1975, **47(11)**, 1752.

WIL82: J.P. Willis, Department of Geochemistry, University of Cape Town, South Africa, National Materials Programme, Final Report, 20 May 1982.

Y

YIN87: X. Yin, G. Schlemmer and B. Welz, Anal. Chem., 1987, **59**, 1462.

APPENDICES

APPENDIX I

1. Atomic Absorption Spectrophotometer

The Perkin-Elmer model 5000 Atomic Absorption Spectrophotometer can be operated in one of three modes:

(i) Atomic absorption mode (AA): background corrector lamp off.

(ii) Background corrected absorption mode (AA-BG): atomic absorption with background correction.

(iii) Background only mode (BG): only background absorption measured.

Peak height or peak area readings are displayed on the digital readout of the spectrophotometer after the selected time interval (seconds) of measurement. The start of integration or peak height measurement is triggered by the furnace programmer.

2. Graphite furnace

The Perkin-Elmer HGA 500 furnace programmer allows up to nine steps of thermal treatment. The temperature (°C), ramp time (seconds) and hold time (seconds) for each step are entered via a keyboard. The flow rates (0 to 300ml per minute) of the internal purge gas and external sheath gas are also entered via the keyboard. Selection of an alternate gas is achieved by pressing the "Alt flow" key in the appropriate thermal treatment step.

A feature of the HGA 500 is the maximum power heating facility with temperature control. This allows rapid heating of the graphite tube, using maximum power, thus maximum speed, to a preselected temperature. Temperature

overshoot is prevented by manual calibration of an optical sensor to detect the end of rapid ramping.

APPENDIX II

Optimisation of furnace operating parameters

The following programmable parameters are available for each thermal treatment step:

(i) Temperature (°C).

(ii) Ramp time (seconds): time taken to reach selected temperature. Maximum power mode is selected by keying in a ramp of 0 seconds for the atomisation step.

(iii) Hold time (seconds): time that selected temperature is maintained.

(iv) Internal purge gas flow rate (ml/min): rates from 0 to 300 ml/min are available. The purge gas can be inert (usually argon or nitrogen) or reactive (usually air or oxygen). The reactive gas is selected by activating the "Alt flow" key on the programmer.

Furnace programs generally consist of three steps:

(i) Drying

Rapid evaporation should occur. Rapid boiling leads to spattering which results in poor analytical precision. For complex samples, two or more drying steps may be required to achieve smooth evaporation. The drying step can be visually monitored by rotation of the furnace unit or with the aid of a dental mirror.

(ii) Ashing

This step is used to remove matrix components which are more volatile than the analyte, thus decreasing the possibility of broad band absorption

interferences. The ashing temperature should be high enough to achieve this, but analyte volatilisation losses should not occur. The ashing temperature is optimised by varying the ashing temperature at a constant atomisation temperature. An ashing curve is plotted (absorbance versus ashing temperature). The optimum ashing temperature is the highest temperature at which no analyte losses occur. The optimum ramp and hold times are determined by monitoring the background absorbance (spectrophotometer in BG mode). With complex samples, multiple ashing steps may be required.

(iii) Atomisation temperature

This should be high enough to completely atomise the analyte. It is optimised by varying the atomisation temperature at a constant ashing temperature. An atomisation curve is plotted (absorbance versus atomisation temperature). The optimum atomisation temperature is the lowest temperature giving the maximum signal. The atomisation time should be long enough to allow the signal to return to the base line. The base line is determined by operating the furnace with no sample. The background at various atomisation temperatures is monitored in BG mode.

A fourth (cleaning) step is often added to remove any residual matrix and to reduce the possibility of memory effects. Occasionally a fifth (cool down) step is necessary with platform atomisation to allow the platform to return to room temperature.